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5. Polymer Coated Fertilizers and Their Scope in Modern Agriculture

Souvik Sadhu

Department of Soil Science and Agril. Chemistry,
Bihar Agricultural University,
Sabour.

Sumit Sow

Department of Agronomy,
Rajendra Prasad Central Agricultural University,
Pusa.

Ritwik Sahoo

Department of Plant Pathology,
Uttar Banga Krishi Vishwavidyalaya,
Pundibari.

Shivani Ranjan

Department of Agronomy,
Rajendra Prasad Central Agricultural University,
Pusa.

Abstract:

Increasing fertilizer prices coupled with lower nutrient use efficiency (NUE) have not only cut down the crop productivity and nutritional quality, but also have severe environmental consequences like greenhouse gas (GHG) emission, ground water contamination etc. Polymer coated fertilizers (PCFs) are promising tool, where the fertilizer is encapsulated with synthetic or natural polymers, which release the nutrient gradually upon decomposition of the polymer by microbial break down. The main advantage of PCFs is that it releases the nutrient over an extended period of time synchronising with the plant demand, thus mitigating environmental hazard and maximizing NUE. In this book chapter, we have tried to discuss, after thorough literature review, about different kinds of slow-release fertilizers (SRFs), their mechanism of nutrient release and commonly used polymers in SRF formulation. Potentials of PCFs in regulating nutrient release, enhancing nutrient uptake and crop productivity has also been dealt with lucidly.

Keywords:

Polymer coated fertilizers, Nutrient use efficiency, Crop productivity

5.1 Introduction:

According to the United Nations (UN, DESA 2019) the world population will reach to around 9.7 billion by 2050. The Food and Agriculture Organization (FAO) has predicted that the world foodgrain production must increase by 70% by the year 2050 to feed this ever-growing population [5]. Unanimously, the world agriculture will face much challenges to accommodate this large population with foodgrains. Fertilizers are one of the most crucial agricultural inputs in order to increase crop productivity [2, 27]. The essential nutrients required for plant growth is supplied through fertilizers, which enhances the crop growth and yield and deficiency of one or more nutrients can result in drastic reduction in yield. Fertilizers can be supplied via soil application (uptake through plant roots) or foliar application (uptake through stomata) [10, 37].

Considering the indispensable role of fertilizers in enhancing crop yield, it is imperative to boost up the fertilizer consumption by the crops [18]. But it is a matter of great concern that very little fraction of the conventionally used fertilizers are taken up by the crops, i.e., 30-35% of nitrogen [9], 10-15% of phosphorus [31], 30-50% of potassium and 1-2% of the micronutrients [12] applied are utilized by the plants and rest are subjected to various losses such as volatilization, leaching, fixation in clay inter-layer *etc*. These unutilized nutrients are not only responsible for economic loss in terms of poor yield, but also leads serious environmental hazards [7]. These include GHG emission, global warming, eutrophication, ground water contamination and so on [33, 38]. So, all these factors in combination, have raised worldwide concern among scientists as well as farmers, which have necessitated development of such fertilizer formulation that can improve crop yield and apparent nutrient recovery on one hand and minimize environmental hazard of the left-over nutrients on the other [6, 35]. One of the recent advancements in this direction is slow-release fertilizers (SRFs) and controlled release fertilizers (CRFs) [16], where the nutrient element is coated with different polymeric substances or some inert, impermeable membrane which, through its various mechanisms, extends the nutrient release time and supresses the nutrient release rate, thereby increasing the duration for which plant roots remain in contact with the nutrient solution. Scientists have illustrated minute differences between these two. In SRFs the release rate of nutrient is mostly unpredictable and determined mainly by soil and climatic conditions, whereas, for CRFs the quantity and nutrient release pattern can be quantified prior to its application [41] although laymen use these two terms (SRFs and CRFs) synonymously as SRFs. These polymers coated SRFs have certain definite characteristics which make them distinctive from the conventionally used fertilizers both in terms of nutrient utilization efficiency and environmental sustainability. These are:

- These enable the growers to manage the rate and timing of nutrient discharge so that fertilizers applied at the beginning of the season can provide the plant roots with nutrients in optimum quantity and in balanced proportion through its controlled agrochemical delivery system [3, 24].
- The extent of nutrient liberation ranges from few weeks to several months depending upon the thickness and degradability of coating material. Release through this extended period minimizes nutrient losses and environmental hazards [4, 25].
- Polymer coated urea have been proven to reduce NO_3^- leaching [45], N_2O discharge [14] and NH_3 volatilization [32].

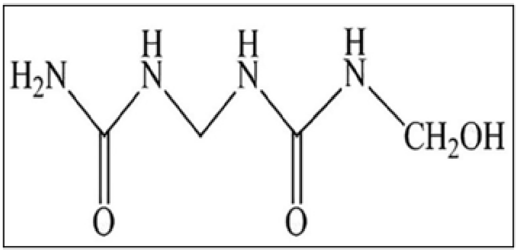
5.2 Slow-Release Fertilizers (SRFs):

SRFs are one of the hotspot research areas now-a-days to combat with the low NUE of the traditional fertilizers and these chemically engineered fertilizer formulations are proving themselves as a ray of hope. They release the plant nutrient gradually through an extended period with the decomposition of the surrounding polymer or inert material through various biotic and abiotic means.

The acceptability of these SRFs obviously depends upon the cost of coating material, their eco-friendliness and degradability. Due to their gradual release pattern, unlike the traditional fertilizers where majority of the nutrients gets discharged within a week of application, neither the plant roots are subjected to toxic nutrient overdose nor the unutilized nutrients can be removed from the root zone. On the basis of the composition of coating material, [39] categorized the SRFs into three broad categories.

5.2.1 Uncoated N- Based Fertilizers:

Oldest category of CRFs where the controlled-release is achieved by increasing the structural complexity of the nutrient element by chemical combination or complexation. Higher structural complexity makes it less accessible to various disintegrating forces and release of nutrient from this chemical complex depends upon available soil moisture, pH, soil temperature, microbial load *etc* [23]. *e.g.*- Urea formaldehyde (Figure 5.1) and Crotonylidene diurea (Figure 5.2)



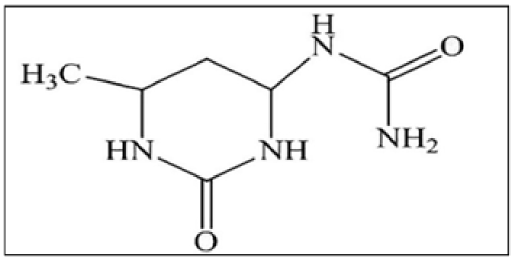


Figure *5.1:* Urea formaldehyde

Figure *5.2:* Crotonylidene diurea

5.2.2 Coated N- Based Fertilizers:

Here the nutrient element is coated by an impermeable material resistant to decomposition by physical, chemical or biological means. This coating, being relatively water insoluble, acts as a physical barrier to the nutrient release on one hand, and supplies additional nutrients on the other. *e.g.,* sulphur coated urea supplies sulphur (S) additional to N, phosphor gypsum coated urea supplies S and Ca additional to N (Figure 5.3). Here coating thickness and durability are the main controller of nutrient release [30].

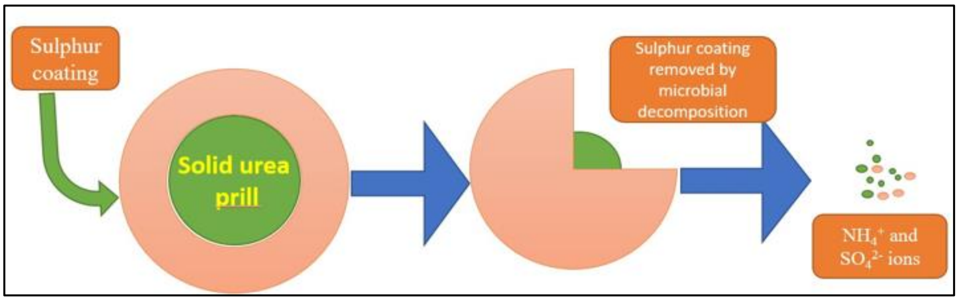


Figure 5.3: Decomposition of sulphur coating and release of N from SCU

5.2.3 Polymer Coated Nutrient Fertilizers:

Polymer coated fertilizers are the latest advancement in the field of fertilizer research, where the soluble nutrient is surrounded by a wide range of polymeric substances, both natural and synthetic. Natural polymers like starch, cellulose, chitosan and synthetic polymers like polyethylene, polyurethane, alkyd resin *etc.* are widely used [41].

Now-a-days super absorbent polymers, a branch of cross-linked hydrophilic polymers, are widely used as a coating material. These polymers, besides controlling the nutrient release rate, can absorb moisture 5-10 times of their body weight and can retain enormous quantity of water. Due to this behaviour, these polymer-based fertilizers are gaining popularity in enhancing the water use efficiency (WUE) too besides NUE. Bio-degradable polymers, unlike synthetic polymers, are eco-friendly and promote soil microbial population by acting as a food and water source for the microbes [23]. Corncob [43] and Cotton stalks [44] are effective source of bio-origin polymers.

5.3 Mechanisms of Nutrient Release:

As already mentioned earlier, the polymer coated SRFs, unlike the traditional fertilizers, release the nutrient in more gradual manner. This release is dependent upon the biodegradability and mechanical properties of the coating material, thickness of polymer coating and different soil properties (temperature, moisture content *etc*).

After soil application of these polymer coated fertilizers, moisture present in the soil penetrates through the polymer coating and as a result the hydrophilic polymers gets swelled up and the encapsulated nutrients become activated. This phenomenon is followed by dissolution of nutrients, development of osmotic pressure and diffusion of the nutrients through the polymer coating gradually over several months, with concentration gradient being the driving force [40].

Meanwhile, these polymers being source of moisture and carbon substrates, are decomposed by soil microbes and complete release of nutrients occur. Several models have also been proposed by various scientists to envisage the kinetics of nutrient release from the polymer coated CRFs such as Fickian diffusion model [11], Higuchi model [29] *etc*. which are beyond the scope of this chapter.

5.4 Polymers Commonly Used in Polymer Coated CRF Formulation:

5.4.1 Synthetic Polymers:

The SRFs can be formulated by using either hydrophilic or hydrophobic polymers. These polymers are based on resin or thermoplastic material. Hydrophobic polymers when used as a coating material, the coating gets porous and partially degraded in soil. Nutrient release through this porous membrane due to diffusion pressure [15]. Hydrophilic polymers absorb water and gets swelled up and nutrients diffuses out as result of dissolution.

A. Hydrophilic polymers:

Hydrophilic polymers (super absorbent polymers) are three dimensional polymers with cross linking networks that are able to absorb and retain water quite a few times of their body weight. Hydrogels are recommended widely as a water saving tool for rainfed farms which run short of soil moisture, and specially in arid regions [46] where they reduce the dependence on irrigation.

Polymer matrix was also prepared from poly acrylic acid (PAA) via solution polymerization technique by [42] for the slow release of potassium-di-hydrogen-phosphate (KH_2PO_4). Polysulfone (PSF) and polyacrylonitrile (PAN) are also used to coat conventional NPK fertilizers for precise nutrient delivery.

B. Hydrophobic polymers:

Hydrophobic polymers, as the name indicate, are insoluble in water due to the absence of polar character. Polyethylene (PE), Polypropylene (PP), Ethylene-vinyl acetate (EVA), Polyurethane (PU), Polystyrene (PS) *etc*. are the mostly used hydrophobic polymers used in CRF formulation [30]. [43] reported that about 80% N was released during 180 days in water at 25^0 C from 100% PE coated fertilizer, whereas, 98% N was discharged during only 98 days in case of 50% PE coating.

5.4.2 Natural Polymers:

Natural polymers are more preferred to their synthetic counterparts due to their renewable origin, easy biodegradability and better stimulative effect on crop yield and soil health. Polysaccharides (starch, lignin, cellulose, chitosan *etc*.) are regarded as the most outstanding category of bio-polymers. [8] prepared a polymer composite from starch-g-poly (L-lactide) and loaded it with urea to use as a SRF. Similarly, [26] formulated a urea loaded SRF where the polymer was synthesized from starch-g-poly (vinyl acetate).

Chitosan is another important bio-origin polymer having antiviral, antifungal properties as well as acts as a source of N [13]. [15] prepared a new nitrogenous SRF formulation from in-situ hydrogelation of chitosan and salicylic aldehyde in presence of urea. Agricultural waste such as wheat straw is also a potential source of raw material for the synthesis of different polymers [17] which have been used as coating materials in SRF formulation.

5.5 Nano Clay Polymer Composite (NCPC) Based Fertilizers:

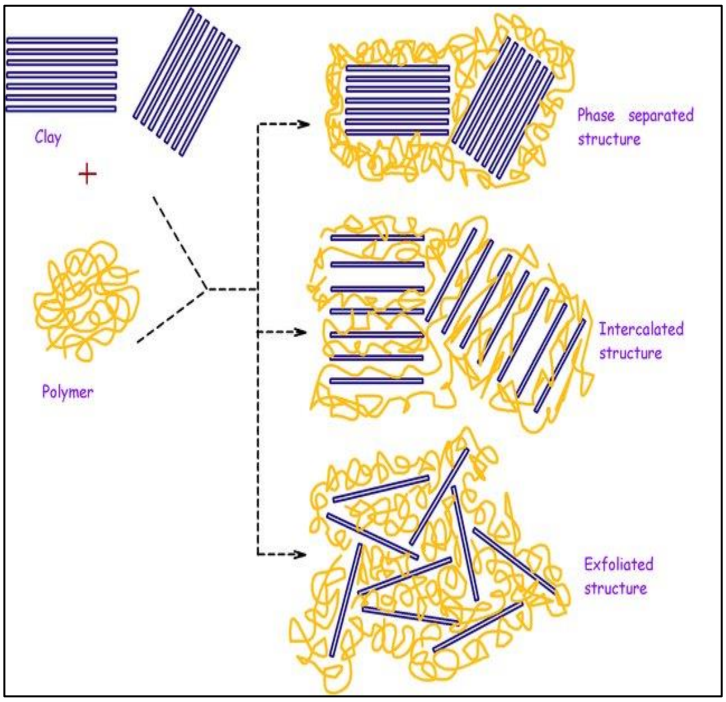


Figure 5.1: Nano clay polymer composite (modified from Mukhopadhyay *et el.*, 2014)

NCPC based fertilizers (Nitrogen- NCPC, Potassium- NCPC, Iron- NCPC, Zinc- NCPC and Multi nutrient- NCPC) are being used widely now-a-days and are making a paradigm shift in the fertilizer industry. In these NCPC based fertilizers, the clay polymer composite is loaded with the nutrient element (either N, K or micronutrients). The clay polymer composite is prepared with acrylic acid-acrylamide as super-absorbent, NNMBAD as cross-linker and nano clay prepared from either kaolinite, illite or smectite as diffusion barrier [21, 36]. The mechanism of this NCPC based fertilizer is to separation and exfoliation of nano clay into its structural units (silicate layers) and formation of cross linkage between these units. When the NCPC is loaded with urea (for N) or micronutrient salt, the nutrient element gets arrested within the cross-linkages.

Prolonged release of nutrient from these NCPC based fertilizer results in higher NUE. [36] in their leaching experiment, found that the cumulative P and total mineral N recovery increased to the extent of (+57.3 and +16.2 %), (+55.2 and +15.4%) and (+88.3 and +27.3%) with the use of fertilizer loaded NCPC synthesized with kaolinite, illite and smectite respectively when compared with conventional fertilizers.

5.6 Effect of Polymer Coated CRFs on Nutrient Release:

[20] conducted an experiment where they prepared zincated NCPC with acrylic acid-acrylamide copolymer using graded amount of clay and nano-clay and compared the release pattern of DTPA-Zn with conventionally used $ZnSO_4.7H_2O$ (Table 1) in two different soil order.

It is clear from the table that $ZnSO_4.7H_2O$ had maintained higher DTPA-Zn at initial period of incubation (15 days) which gradually decreased afterwards. Contrary to this, reverse trend was noticed in case of polymer composites, where lower DTPA-Zn

Table 5.1: Release of DTPA-Zn as affected by different polymer combination

	DTPA- Zn content in soil-I (ppm)				DTPA- Zn content in soil-II (ppm)			
Treatment	**15 days**	**30 days**	**45 days**	**60 days**	**15 days**	**30 days**	**45 days**	**60 days**
T1	1.86	2.84	5.33	6.53	1.87	2.68	4.44	5.53
T2	1.66	2.46	4.71	6.08	1.78	2.49	4.16	5.13
T3	1.44	2.06	4.61	5.52	1.33	2.26	3.94	4.27
T4	1.14	2.28	4.96	5.79	1.5	2.68	4.13	5.13
T5	1.12	2.39	4.59	5.41	1.11	2.42	3.53	4.47
T6	0.95	1.97	4.34	5.17	0.87	2.12	3.07	3.87
T7	5.12	3.31	2.97	2.5	5.01	2.03	2.82	2.43
CD (p= 0.01)	0.17	0.11	0.17	0.17	0.16	0.05	0.07	0.08

[T1: 8% clay; T2: 10% clay; T3: 12% clay T4: 8% nano clay; T5: 10% nano clay; T6: 12% nano clay and T7: Conventional Zn sources ($ZnSO_4$. $7H_2O$).] -Source- [20]

content at the initial period was followed by higher content of the same at the later period of incubation (Figure 5.5, 5.6). The role of polymer composites in decelerating Zn- release increased with increase in clay content and was more conspicuous when nano-clay was used as diffusion barrier in the polymer matrix, which was attributed to their better exfoliation tendency. It makes clear sense that at initial period of plant growth, the root density being less, plant cannot uptake much nutrient. The uptake capacity increases gradually with the development of root system. This explains why micronutrient use efficiency is limited only to 1-2% using conventional micronutrient fertilizers and how polymer composite fertilizers can play a crucial role in improving the NUE.

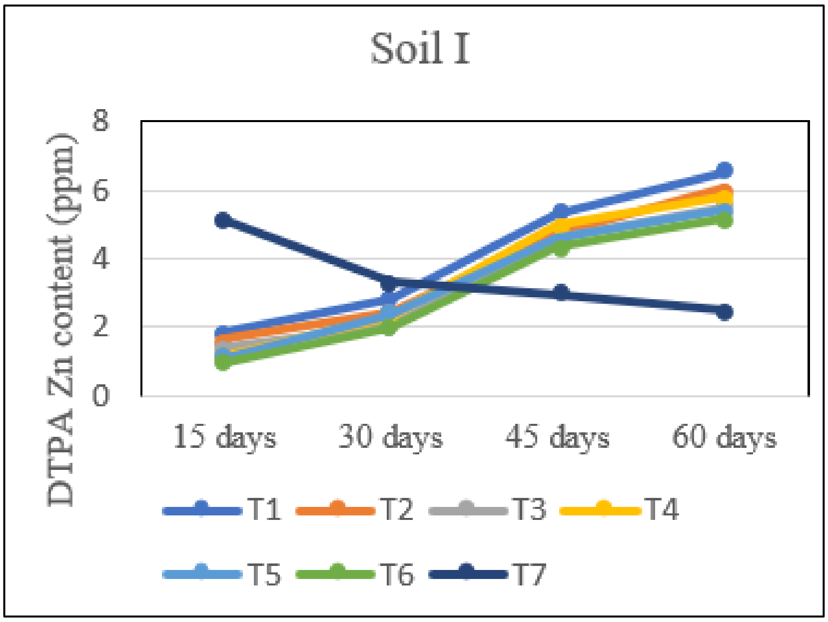


Figure 5.5: Release pattern of DTPA- Zn in Soil-I

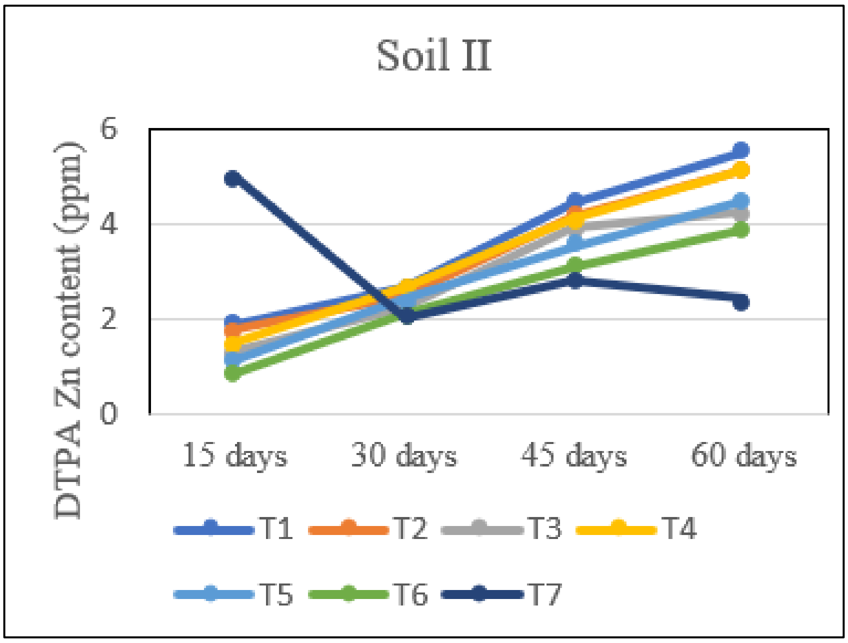


Figure 5.6: Release pattern of DTPA- Zn in Soil-II

Similar kind of experiment was conducted by [34] on P supplying capacity of indigenous rock phosphate (RP), (from two sources viz., Udaipur and Purulia) as these are easily available but most of them are of low solubility and their P concentration is also less [19], which leads to importation of RP from foreign countries involving higher cost. Citric acid loaded in NCPC was applied to solubilize RP and release plant available P.

The P supplying capacity of RP was compared with DAP in a greenhouse experiment on wheat followed by rice (Table 5.2).

Table 5.2: Yield and P uptake by wheat and rice as influenced by rock phosphate treated with citric acid loaded NCPC

	Total yield (g/pot)		Total P uptake (mg/kg)	
Treatment	Wheat	Rice	Wheat	Rice
URP+ CA-NCPC	15.98	15.70	17.11	16.91
PRP+ CA-NCPC	15.89	16.19	16.95	18.02
DAP	16.08	15.40	18.05	16.90
Control	12.72	11.11	11.91	6.80
CD (0.05)	0.25	1.60	1.15	2.46

[URP- Udaipur rock phosphate; PRP- Purulia rock phosphate; CA-NCPC- Citric acid loaded nano clay polymer composite; DAP- Di ammonium phosphate] Source- [34]

The rate of P release due to solubilization of RP was found to be good enough to maintain available P content at par with DAP. Citric acid loaded NCPC acted as a slow-release P fertilizer as evidenced from Table 5.2. Yield of both rice and wheat as well as total P uptake by these crops due to RP application was comparable to DAP. Higher rice yield in RP treated pots compared to DAP indicates the better residual effect of RP as a phosphorus source.

5.7 Future Direction of Research:

The research about polymer coated CRF is still in its budding stage and many more facets are yet to be unveiled. Future researchers should focus on developing inexpensive CRFs which are eco-friendly and do not have any detrimental effect on soil health as well as on the environment. This novel technology can only be disseminated from laboratory to farmer’s field with multi-locational field trials so that farmers are compelled to acknowledge the real practical advantage of this novel technology. One more point to focus on is upscaling the production of this CRFs on an industrial scale. The residual effect of CRFs applied in a crop, if any, on the subsequent crop also needs to be explored.

5.8 Conclusion:

The traditionally used fertilizers leave environmental footprint by polluting ground water, emitting greenhouse gas *etc*. Moreover, plants cannot utilize these nutrients to full extent. Polymer coated fertilizers are advanced technology where the nutrients are supplied through controlled agrochemical delivery system by virtue of its barrier property towards nutrient diffusion. This results in better recovery efficiency of applied nutrients and ultimately crop growth and yield. Nutricote, Osmocote, Polyon *etc*. are widely used coating material used for this purpose. NCPC based Zn containing micronutrient fertilizer results in gradual Zn release, which makes it more accessible to plant roots. Researchers are engaged in evaluating the effect of polymer coated CRFs on various crops and cropping system as well as on the NUE of various nutrients under diverse soil and climatic conditions.

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