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A REVIEW ON CHANGES IN FERTILIZERS: FROM COATED CONTROLLED RELEASE FERTILIZERS (CRFS) TO NANOCOMPOSITES OF CRFS

NALINI SHARMA & AJAY SINGH

Uttaranchal University, Dehradun, India

ABSTRACT

Past decades have seen a keen-edged bloom in Agro-Technical aspects. The expansion of global population and the inflation in global food demand has given rise to multitudinous research in the agronomic sector, especially in the domain of fertilizers. The use of fertilizer in agricultural field is essential for the plant growth, but excess amount of pure chemical contents used in them can pose a serious threat to all living beings and also to the environment. In order to reduce this chemical exposure, the use of materials coated Controlled Release Fertilizer or CRFs became quintessential. The coating of materials outside the fertilizer enables the active content of fertilizers to release in a gradual or delayed manner, in accordance to the plant demands. The longevity of CRFs depends upon the thickness of coating material, which can either be organic or inorganic. Temperature and moisture are the greatest players which influence the workability of coated CRFs. Further improvisation in CRFs is done with the introduction of Nanotechnology in agricultural research, as it has put forth innumerable advantages with respect to development. 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. The present study covers the extensive evolution of controlled release fertilizers, to the modern and smart Nanotechnology inspired controlled release fertilizers.

KEYWORDS: CRFs, Urea, Kaolin, Montmorillonite & Nanofertilizers

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Original Article

1. INTRODUCTION

The term Agriculture is the anchorage to economy of any country. Henceforth, it is highly required to improvise technical changes in the arena of agricultural sector, which plays the pivotal role in generating a vast and versatile range of employment as well as serves as the fine line in meeting the Global Food Requirements. With the evolution of highly advanced and ever expanding human civilization, the issue of 'Food Security' emerges as the overruling subject which offers a wide spectrum of scope in research for the same. Other major factors, which pose a threat to Global Food Security are, urbanisation, diminishing of agricultural land due to industrialisation, natural calamities which erode productive land as in flood prone areas and also desertification. Multifarious research has already been conducted in this vast exploratory field but it still offers a great scope for innovations to researchers. There exists a huge gap between the vast domains of fertilizers and Agriculture as both of them show synergism. The use of traditional fertilizers, which are mostly the uncoated Nitrogen based fertilizers, is not as effective for modern day agronomics as it once used to be. The major reason for the same being the low uptake of applied nutrients by the plant. Out of all, Urea is the major member in fertilizers used worldwide, because of its high Nitrogen content which is the most important plant nutrient. But, the traditional practice of direct application of

urea does not provide for the complete nitrogen requirement of the plant, as it is lost mostly because of leaching and volatilization. And so, various studies got triggered and gave rise to the evolution of traditional fertilizers to Controlled Release Coated Fertilizers (CRCFs). CRCFs have seen an extensive study for the formulation of coating material ranging from those based on sulphur to polymer based super absorbents, bio-composites and others.

CRCFs comprise of a coating over the active material, usually the desired fertilizer granule. The coating is done to ensure a gradual release of the nutrients from the active core so that the total nutrient demand of the plant with time is fulfilled. The plant in initial stages of growth requires fewer nutrients, and so, the coating has to be designed in a manner which would start the dissolution very gradually and would last up to a considerable period of time for the plant. But, with the passage of time and ever enhancing food demand, the agro-sector still lags behind in terms of efficient commercial grade improvised fertilizers, despite the numerous researches carried on formulating coated slow/controlled release fertilizers. With the emergence of Nanotechnology as a booster for various applications in almost all the fields, even the agriculture sector is not behind in experiencing its beneficiary effects. With the due course of time, it is evident that Nanotechnology can serve the growing demand of a better agro-chemical, and hence will also fuel the rigorous research going on in the same direction. The review herewith encompasses the evolution of CRF nanocomposites from traditional fertilizers via coated CRFs as: Traditional fertilizers; coated controlled release fertilizers (CRFs) and Nanocomposites of CRFs.

1.1. Taxonomy of Controlled Release Fertilizers

On the basis of coating and nutrient composition, CRFs can be divided into three major categories viz. Uncoated Nitrogen based fertilizers which are most traditional ones and comprise mostly of chemically bound Urea; Secondly, Coated Nitrogen based fertilizers with sulphur coated urea as the first member in the category. They present the benefit of monitoring the release by alteration of coating thickness and lastly, the polymer coated multi-nutrient fertilizers which are the newfangled innovation in the arena of fertilizers, which is majorly used in horticultural plant production. They consist of nutrient core enveloped by polymer coating in which each coated particle is called Prill. Release of nutrients through them is subject to chemical composition and thickness of polymer coating [1].

Another comprehensive approach categorizes CRFs in a more intricate and diversified manner highlighting their major usage and physical forms [2, 3, 4, 5]. The authors classified the CRFs into three broad scales as: Firstly, Organic compounds which are further sub-divided on the basis of source, from which, they are acquired as Natural organic compounds like sewage sludge or animal manure and Synthetic Organic-Nitrogen compounds which comprises of condensation products of urea and acetaldehyde further classified as : Biologically decomposing compounds like urea formaldehyde (UF) and Chemically decomposing compounds like isobutyledene-diurea (IBDU) and urea acetaldehyde/cyclo diurea (CDU). Secondly, Water soluble fertilizers with physical barrier to control release in either of the forms like Coated Granules Coated with a hydrophobic polymeric material which may be Organic Polymer coated e.g., thermoplastics, resins etc. or Inorganic Material coated e.g., sulphur and other minerals coated; Secondly, Fertilizer matrices with dispersion of active nutrients of fertilizer through a hydrophobic material, which helps in retarding the dissolution of fertilizer further grouped as Hydrophobic Matrix Material: Example, rubber, polyolefin etc., and Hydrophillic hydrogel: Dispersion of fertilizer through hydrogels is disrupted by their ability to retain water, or in other words their tendency to swell. And lastly, Inorganic low solubility compounds, which include Metal Ammonium phosphates (KNH4PO4) and Partially Acidulated phosphate rock (PAPR).

1.2. General Mechanism for Controlled Release of Nutrients from Fertilizers

The measurement of efficacy of a CRF is based on the intricate study and understanding of the mechanism it follows, which depends on a number of related factors like the thickness and nature of coating material, type of CRF used, and also the agricultural conditions in which it is to be applied. Though there are numerous mechanisms already cited in the literature, but there still exists a wide scope in the same. A multi-stage diffusion has been proposed by Shaviv [2] and Liu[4], which depicts the release mechanism through the following steps after the application of coated CRF: Penetration of irrigation water into the coating; Dissolution of nutrients partially; Building up of osmotic pressure within the fertilizer granule and Swelling up of granule by either of the two processes i.e., Bursting of granule and release of nutrients all at once, when the threshold membrane resistance is overcome by osmotic pressure called the Failure or Catastrophic mechanism, generally depicted by delicate coatings like those of Sulphur or Diffusion mechanism, wherein the membrane stays strong against the developing pressure and releases the nutrients gradually as a consequence of concentration or pressure gradient or the combination of both as depicted by polymeric coatings.

Release mechanism is directly dependent upon temperature and moisture content [5]. A similar inference was drawn by a study on Carboxymethyl starch, ammonia, urea, acrylic acid and diammonium phosphate which were used to prepare NP fertilizer depicting properties like super absorbency and conservation of moisture. Optimization was done on certain factors which affect the properties like cross linker and initiator amount and also neutralization extent of acrylic acid over absorbency of water. Product showed 22.6% N and 7.2% P. Also, the product showed enhanced capacity for retaining moisture, which subsequently retarded the release of nutrients and water absorbency of 85(g g-1) times the original weight in tap water [6].

2. NEED OF CRFs

There exists a serious situation in agriculture, when the estimation of total applied nutrients and total nutrient uptake by plant is done. After the application of nutrients to the soil, the plant has to compete with soil micro biota and certain other ongoing chemical reactions for the same. Also, it is a major case that the plant nutrient demand at various stages is not fulfilled by traditional fertilizers, and so CRFs come up as the best contenders which aid in nutrient loss reduction, and also save the amount of labour which is otherwise needed in case of traditional fertilizers as they are required to be applied again and again after a certain interval of time, unlike CRFs. Also, CRFs are mostly centred on reduction in nutrient leaching and improvement in the total nutrition taken up by the plant from the soil. CRFs also hold well in conditions of sandy soils, which do not have efficient water and nutrient binding properties [7]. The use of CRFs however depends on the type of crops, cropping season duration and also on demand of nutrients by the crop [8].

2.1. Overview on Coated CRFs

Production of CRFs has evolved manifolds in the past years. A range of binding materials have been used in formulating various types of CRFs which have shown appreciable results in terms of applicability and efficacy. Though other nutrients also play a major role in the productivity of plant, Nitrogen emerges as the major player in the same. And so, its dominant source, Urea has grabbed the major attention for the formulation of modified new-age fertilizers. The most substantial work in the same direction is claimed to be done for Tennessee Valley Authority (TVA), USA [9], wherein, the author presented a highly efficient and economic method for large scale production of sulphur coated urea granules. Apart from Nitrogen, Sulphur has emerged as an active participant for CRF formulations, as it is also

an active secondary plant nutrient as well as shows good fungicidal activities. It also counteracts upon soil alkalinity through its acidic nature; is cheap available material and acts as anti-caking agent for certain fertilizers. Also, its coating is biodegradable in comparison to the polymeric materials used for CRFs [13, 10]. But, the drawback of using sulphur-only coating is that, due to the crystalline nature of sulphur, microscopic pores get developed in the coating which enhances its brittleness [11, 12]. Because of its larger size, its coating shows low levels of adhesion to the surface of urea [10]. Therefore, sulphur only coatings are not much efficient and needs to be combined with other coating materials.

2.1.1. Urea Based Coated CRFs

Some of the prominent researches based on varied binding and coating materials for making Urea based CRFs is compiled herewith.

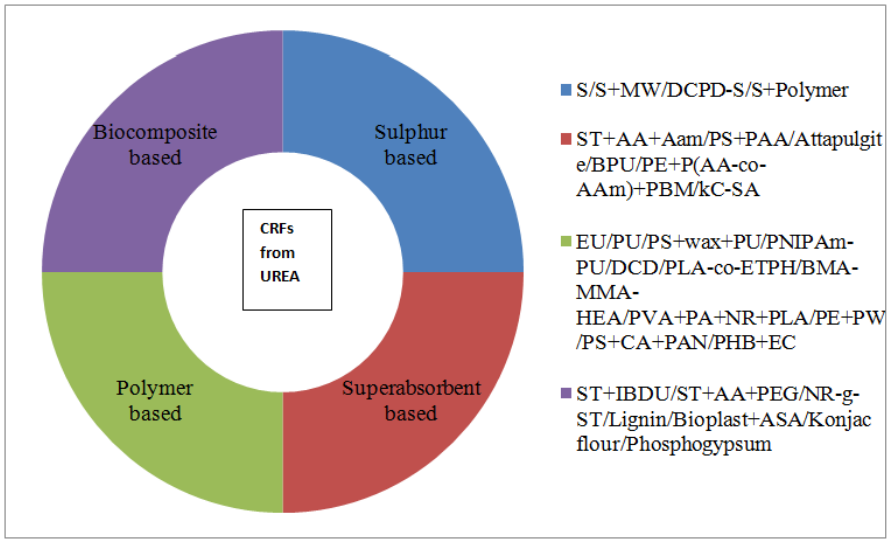

Figure 1: Overview of CRFs from Urea

Table 1: Description of above mentioned combinations of CRFs from Urea

Coating/Binding Material Used	Commercial Name	Methods	Research Findings
SULPHUR BASED			
S	Sulphur only coating	Urea granules impregnated by petroleum by-product as sealant which stopped urea dissolution via filling of small channels through capillary action. Spray coating of urea with sulphur and with plasticizers like polyethylene or polyvinyl acetate [9].	24-hour dissolution test in water showed oil only coating to be ineffective towards water permeability unlike sulphur-only coating which was slightly effective. Combination of both with oil to sulphur ratio of 3:21 proved to be most effective with only 1% dissolution in 24 h.
S+MW	Sulphur & Microcrystalline wax	Plasticizers induced tackiness to the product which led to use of microcrystalline wax. Urea granules sprayed with molten sulphur followed by pouring of microcrystalline wax coupled with 0.5-2% microbicides like coal tar and pentachlorophenol to counteract attack by bacteria. 1% kaolin clay used to enhance the flow[11,13] Spouted bed of urea coated with sulphur subjected to fluidizing air at 80°C with flow rate of 0.65m^3/min and 208kPa pressure [10].	24 h dissolution test – 3.5-4.2% (due to small size of particles) <24 h Dissolution test- 0.8-1.1% Smaller particles showed greater dissolution rates because of grater surface to volume ratio. Thinner coatings showed higher dissolution rates. 30% dissolution of urea in 7-day trial (Urea release by 250g sample tested in 250 ml water at 100°F for seven days)

Table 1: Contd.,			
DCPD-S	DCPD modified sulphur coated urea	Mixing of DCPD and sulphur at higher temperature for 1-6 h done to yield DCPD-modified sulphur which is then coated over urea [14].	Deionised water taken in a beaker covered with polyethylene for evaluation of release rates. Periodic removal of fixed amount of water with replacement with fresh water done to estimate nitrogen concentration via spectrometry. 7 day tests revealed 53.5% dissolution unlike sulphur only coated urea which showed 83% dissolution.
S+Polymer	Sulphur & Polymer	Spray coated sulphur in rotary drum over preheated urea granules in fluidized bed and diethylene glycol triethanolamine polyol and diisocyanate monomers sprayed over resulting granules [15]. Expansion of above technique to produce triple layer coated urea. First coating of 4, 4-diphenylmethane diisocyanate, triethanolamine and diethylene glycol polyols; second coating of sulphur and final coating same as the first one. Coatings done by on-surface polymerization [16].	7-Day dissolution test revealed 38% dissolution. Release period of nutrients got doubled than that found by previous technique.
SUPERABSORBENT BASED			
ST+AA+AAm	Starch, Acrylic acid & Acrylamide	Inner shell of starch and outer layer of acrylic acid and acrylamide formed double coated urea granules. Absorption of water causes formation of hydrogel which enhances slow release of urea which gets dissolved in hydrogel matrix [17].	10% dissolution in 2 days; 15% dissolution in 5 days and 61% dissolution in 30 days.
PS+PAA	Polystyrene & Polyacrylic acid	Inner layer of polystyrene and outer layer of polyacrylic acid to formulate double coated urea [18].	Controlled release enhanced by outer coating. Water retention observed which is necessary for effective irrigation.
Attapulgite	Attapulgite	Attapulgite (inert towards urea) matrix used for fertilizer core. Two layer coating: Ethyl cellulose + plasticizer (inner coat) and Sodium carboxymethylcellulose+ hydroxyethylcellulose (outer coat) [19].	8.7% release after 24 h soil incubation (slow release by ethylcellulose coating). Consistent release during 2-5day. In last stages attapulgite enhanced slow urea release by absorption of remaining nutrients.
BPU	Biopolyurethane	Biodegradable coating. Obtained from liquefied corn Stover (inner coat) and acrylic acid modified superabsorbent material (outer coat)[20].	Increment in coating mass enhanced controlled release.
PE+P(AA-co-AAm)+PBM	Polyethylene, Poly(Acrylic acid-co-acrylamide) & Poly (butyl methacrylate)	PE-inner coating- slow release film; P (AA-co-AAm)-middle layer-water retaining superabsorbent and PBA-final layer- protection to middle layer [21].	Release by 25µm thickness- 4.2%, 38%, 56% for 1, 7 and 14 days & that by 50µm, 0.1%, 10.1% and 10.3%. Release increased at high temperature.
kC-SA	k-Carrageenam (polysaccharide from red sea weed)-Sodium alginate (natural anionic macromolecule)	kC-SA used as inner coat and kC graft copolymer with polyacrylic acid and celite used as outer coating to double coat urea. Mechanical strength of coating improved [22].	39%, 72% and 94% release in soil incubation at 2, 5 and 25 days.
POLYMER BASED			
EU	Eudragit L30-D55 (methacrylic acid copolymers)	Eudragit(16.7%)+polyethylene glycol(0.75%)+triethyl citrate(0.5%)+esthearate of Mg(1%)+titanium dioxide(1.8%)+ pigment(0.2%)+talc(2.75%)+water(76.3 %)[23]	Uniform coating film produced due to formation of small droplets at enhanced atomizing air pressure. Increase in thickness of coating also showed enhanced controlled release features. Not effective for soils with pH>5.5 due to thick coating.

Table 1: Contd.,			
		Eudragit(25%)+polyethylene glycol(0.75%)+triethyl citrate(0.5%)+esthearate of Mg(3%)+titanium dioxide(1.8%)+pigment(0.2%)+talc(3%) +vinasse(65.75%)[24]	Volatilization of nitrogen reduced up to 57% with the use of vinasse, an effluent from ethyl glycol production rich in N, P, Ca and Mg needed for plant growth.
PU	Polyurethane	Isocyanate, polyols and wax added to urea granules in rotating drum to produce relatively thin 10-15 micrometer coating of polyurethane[25].	Dissolution tests showed: 10% dissolution (10 days); 70-80% dissolution (30 days); Total release (by 45 days).
PS+wax+PU	Polystyrene(waste) ,wax & Polyurethane	Polyurethane prepared by agitating diphenylmethane diisocyanate and further mixing with polystyrene dissolved in ethyl acetate. Wurster fluidized bed used to spray coat urea granules with this solution [26].	No substantial effect of wax coating. Release rate inversely proportional to coating thickness. Polyurethane increased controlled release.
PNIPAm-PU	Poly(N-isoproppylacrylamide)-co-polyurethane	Synthesis of Amino terminated PNIPAm (NH_2-PNIPAm) done by radical polymerization of N-Isopropyl acrylamide using potassium persulfate as radical initiator. 2-aminoethanethiol hydrochloride used as chain transfer reagent. Isocyanate Terminated Polyurethane (NCO-PU-NCO) prepared from Poly (1, 4-butylene adipate)diol. NH_2-PNIPAm and NCO-PU-NCO reacted at 90° to form PNIPAm-PU which was then used to coat urea granules [27].	Bursting effect reduced as polymer coating so produced efficiently withstood the osmotic pressure.
DCD	Polyolefin & dicyanidamide	Urea granules placed in concrete mixer and sprayed with DCD solution in dilute phosphoric acid. Polyolefin + DCD urea granules synthesized in same manner [28].	Most efficient granules were Polyolefin+DCD coated regarding controlled release and also kept soil nitrogen intact.
PLA-co-ETPH	Poly(Lactic acid-co-ethylene terephthalate)	Comparative study of polylactic acid coated urea granules done with those coated with PLA-co-ETPH (solution in chloroform sprayed over urea granules) [29].	Nature, concentration, surface morphology and percentage of coating thickness indirectly proportional to controlled release.
BMA-MMA-HEA	N-butyl methacrylate, monomethylacrylate & 2-hydroxyethylacrylate	Monomers stirred under nitrogen supply and solution of benzoyl peroxide in ethyl acetate added to the same. Coating solution so obtained sprayed on urea granules on fluidized bed[30].	100% dissolution in initial eight days. Addition of 10% paraffin wax improved controlled release as: 1.54% at 24h and 78.77% at 28 days.
PVA+PA+NR+PLA	Polyvinyl chloride, Polyacrylamide, Natural rubber & Polylactic acid	Compound fertilizer synthesized with a combination of polymers as coating material [31].	Controlled release properties enhanced.
PE+PWs	Polyethylene & Paraffin wax	Used for NPK fertilizers [32].	Improved release patterns.
PS+CA+PAN	Polysulfone, cellulose acetate & polyacrylonitrile	Used for NPK fertilizers [33, 34, 35].	Improved release patterns
PHB+EC	Polyhydroxybutyrate & ethyl cellulose	PHB dissolved in chloroform and EC dissolved in acetone to form coating solution. Immersion and manual spraying done over urea granules [36].	Complete dissolution observed within 5 min. Not suitable for agro-use.
BIOCOMPOSITE BASED			
ST+IBDU	Starch & isobutylidendiurea	IBDU-inner layer and starch+wax powder outer layer. Sigmoidal release pattern observed (initial slow release and then continuous increase) [37].	Outer impermeable layer caused sigmoidal release and hence effective for slow urea release.

Table 1: Contd.,			
ST+AA+PEG	Starch, acrylic acid & Polyethylene glycol	Homogenous mixture of the combination obtained and spray coated on urea over fluidized bed with top spray of starch based coating material [38].	Slow release pattern enhanced. Release increased at elevated temperatures.
NR-g-ST	Potassium persulphate modified starch & Natural rubber	Starch modified with potassium persulfate and graft polymerized with NR to form NR-g-ST. Urea granules immersed in the aforementioned formulation for coating [39].	21% release observed in 24h. Hydrophobic natural rubber core shell remained after nutrient release.
Lignin	Lignin	Lignin mixed with urea and immersed on hydrostatic silicon oil bath to yield glass like formulation which was then milled to desired particle size [40].	Release rates initially slow but increased gradually. Coating thickness inversely proportional to release patterns.
Bioplast+ASA	Soda flax Lignin (Bioplast), Acronal (Plasticizer) & Alkenyl succinic anhydride (cross-linking agent)	At 70°C urea granules sprayed with 25% mixture of coating combination in rotary pan [41].	Coating thickness and uniformity played important roles in release patterns.
Konjac flour	Konjac flour	Urea pallet moulded by heat to cake and soaked in polyether+water+silicon oil+catalyst. Toluene diisocyanate and konjac flour added simultaneously till white solution obtained. Urea pallet coated with white solution and dried [42].	Sample placed in soil with 500ml extra water. 20% release-8 weeks due to swelling of konjac flour. Release increased to 80% due to microbial degradation of konjac flour.
Phosphogypsum	Phophogypsum	Dry coating- Phosphogypsum+ Neem oil+ linear alkyl benzene; Wet coating- same combination + water [43].	Sulphur supplement added by phosphogypsum is better for soil as it does not alter soil pH unlike sulphur.Wet coating found to be more efficient.

2.1.2. Miscellaneous Types of Fertilizer Based Researches for Coated CRFs

In their studies, Shaviv et al., have shown the beneficiary implications of CRFs stating that there does exists a competition for nutrients between soil microorganisms and plants. Also, nutrient release by fertilizer should be in accordance to the plant requirement[44]. In the later studies, it has been shown that controlled release Nitrogen (CRN) fertilizers, which show burst effect give high initial Nitrogen release which causes 45-50% of its loss. While in the fertilizers showing tailing effect the loss reduces after 40-60% of loss. But both the effects cause low N uptake by plants. But, it is not the case with sigmoidal release pattern without tailing effect, which reduces Nitrogen loss with subsequent increase in its uptake by plant[45]. Further, a new controlled fertilizer is formulated in the form of dry mixtuire along with a thickner and sealed in a non-permeable membrane having one opening which firstly allows diffusion of water into the dry mixture and release of nutrients by diffusion or convective flow. Results reveal that increased Nitrogen solubility increases burst effects; increasing the thickner amount slows the nutrient release by slowing the rate of wetting and reduction in opening diameter also reduces the wetting of dry mixture and also the release[46]. Another study on CRFs is done by penetration of water into dry mixtures and formation of gel by polymers. The study highlights the effect of vapour and flow of fluid in the wetting process of CRFs composed of Urea/KNO_3 and Polyacrylamide(PAM) mixture. Mathematical evaluation of study based on liquid flow and vapor impact in dry conditions showed that transportation and vapor adsorption affect wetting patterns differently for liquid flow and vapor flow[47].The usage of solid fertilizers is also presented for single granules of CRFs coated with membrane which depicted complex and non-Fickian nature. Three stages are involved in the process viz. lag period of water penetration into the granule coating and dissolving the solid fertilizer partly; linear release period when water penetrates into the granule and nutrient releases out of it, keeping the

volume constant and lastly, decaying release period when the granule concentration lowers. Complex and sigmoidal release patters are shown by the model, which is positive for agriculture and environment[48]. Release through polymer coated fertilizer (PCF) is also studied through release of nitrate using a generalized regression neural network (GRNN). Factors affecting controlled release like membrane thickness, granule radii, nutrient concentration and temperature are taken as input vectors in the model. GRNN model depicted the impact on superiority in terms of various factors as: membrane thickness>temperature>granule radius> saturated nitrate concentration[49].

Apart from Urea only formulations for CRFs, studies have also been done taking into account other nutrients also like calcium, potassium, phosphorous etc. which are being required for plant growth. It's an evident fact that the enhancement of soil fertility can be done by providing the soil with the required nutrients to meet the physiological need of the plants. Hanafi et al., prepared a controlled release compound fertilizer using 15% N, 2% P, 16% K, 4% Ca, 1% Mg and 0.1% Cu coated with Polyvinyl Chloride, natural rubber, polyacrylamide and polylactic acid. The various polymer coatings showed the thermal-oxidative stability at 300°C in the order: NR>PLA>PVC>PA. It is inferred that differences in polymer characteristics act as a fountainhead in preparing coated compound fertilizers to meet the basic plant requirements [50]. Also the rate of release of macronutrients comprising the core of coated fertilizer is affected by physical parameters of the coatings [51]. It is justified by study carried out by coating commercial fertilizer NPK 6-20-30 with Polysulfone (PSF), Polyacrylonitrile (PAN) and Cellulose acetate (CA). The study brings to light that PSF and PAN aid in slowest release of potassium. CA coatings present the same inference for nitrogen. PSF excelled in being the slowest to release the fertilizer nutrients with lowest porosity coating synthesized using 18% solution of PSF. Chang-wen-Du et al., also presented experimental findings on NPK CRFs based on two coated compound CRF in free water, sand saturated with water and sand at field capacity. The following release pattern was observed starting from the fastest: Nitrate> Ammonium> Potassium> Phosphate; wherein Phosphate being the slowest presented 45-70% slower rate in free water than in nitrate. Lower solubility of ions with Phosphorous is given as an assumption factor for the slow release. Release pattern in different set of conditions is found to follow the order: Free water> Saturated sand> Sand at field capacity. It is observed that an increment in temperature from 20°C to 40°C increased the rate of linear release of nutrients [52]. Lubkowski et al., used a biodegradable copolymer of poly (butylenes succinate) and butylenes ester of dilinoleic acid (PBS/DLA) as a coating material for the formulation of controlled release NPK fertilizer. The paper presents an intricately conceptualized model, which depicts the nutrient release mechanism from the prepared NPK fertilizer, once water has penetrated into the granules. Also, the diffusion properties and diffusion coefficient of the release of nutrients through the polymer layer in water are also studied which reveal a positive result [53].

With further evolution of research in the direction of coated fertilizers, it became evident that the type of coating materials for fertilizers, and their basic properties play a pivotal role in the release pattern in CRFs. Addition of appropriate amounts of macromolecule water-repellent materials and biodegradable starches in the coatings could pose a remarkable enhancement in mechanical properties, hence affecting the release rate of nutrients up to significant levels [54]. Efficiency of a CRF is judged not only on the basis of the amount of nutrient it would release but also its capacity to hold water and keep the soil moisture intact. Efficient slow release effects and also soil moisture retention is achieved by the studies carried out by M.liu et al., which presented efficacious utilization of fertilizers and also presented judicious use of water resources by the development of superabsorbent slow release nitrogen fertilizer (SSRNF). SSRNF so developed would be a promising material for drought-prone areas, where water availability is scanty. N, N-methylene bisacrylamide is used as a cross-linker to prepare SSRNF from partially neutralized acrylic acid through inverse suspension polymerization.

The results show nitrogen content in the synthesised SSRNF to be 22.7% with 965gg-1 water absorbencies in distilled water and 185gg-1 in tap water [55]. Another study with similar objective for formulating an agro-friendly non-toxic product is done by developing a new superabsorbent potassium silicate fertilizer (SRPS) with core/shell morphology keeping the maximum usage of fertilizer and water retention into peer consideration. The core is formulated with potassium silicate in alginate matrix. The shell consisted of poly (acrylic acid-co-acrylamide)/Kaolin (P (AA-CO-AM)/Kaolin) superabsorbent polymer. The product is found to contain 26.6% K_2O and 10.4% SiO_2. Product depicted the water absorbency of 85 times its own weight within 90 minutes at room temperature when swelled with tap water. The product also showed positive results for release characters and water-retention ability [56]. For an efficient and qualitative crop yield, the quality of fertilizer matters but it is majorly affected by the fertilizer utilization capacity of soil and also the water retention in it. Keeping the view in centre, Lan Wu et al., synthesized a novel compound fertilizer comprising of Nitrogen, Phosphorous and Potassium coated by using Chitosan. They formulated a three layered structure for the same with water soluble NPK fertilizer granule as the core, followed by Chitosan inner coating and lastly poly (acrylic acid-co-acrylamide) (P (AA-Co-AM)) superabsorbent polymer as the outermost layer. Product shows 7.98% K (by K_2O), 8.14% P (by P_2O_5) and 8.06% N with effective water absorbency of around 70 times its own weight, when in tap water for 90 minutes. Study of slow release of nutrients and water retention capability of the prepared fertilizer is also done, which gives better results and being degradable in soil, the product presents a wide scope of use in agriculture [57]. To enhance phosphorous release, a Superabsorbent polymer based preparation on sulfonated corn starch/ poly (acrylic acid) using phosphate rock (PHR) in order to overcome its hard texture and failure in complete utilization by plants as a fertilizer is studied [58]. Sulfonated corn starch (SCS) is used to disperse PHR in SCS/PAA. Further, a solution of PHR and KOH is prepared by mixing them in acrylic acid solution for obtaining phosphorous (P) and potassium (K) as nutrients form them, respectively. The paper presents an in-depth investigation on P and K release behaviour from SCS/PAA/PHR, and also effect on absorption capacity of water of the superabsorbent, which shows maximum swelling capacity in distilled water with 0.9 wt% NaCl solution that reached 498 gg^{-1}.

Singh et al., focused on modification of thiram release, which is a dithiocarbamate fungicide, from the beads of starch-alginate in order to reduce environmental pollution due to agro-practices. Kaolin and Bentonite are used in bead formulations as adsorbents and beads of varied compositions in context to amount of superabsorbent are synthesized. Evaluation of beads is done on the basis of several characteristics like the mechanism of diffusion of thiram from them, size of beads and their swelling percentage. FT-IR, SEM and thermogravimetric studies are used for the characterization of synthesized beads. The authors observed in the study that the release followed non-Fickian diffusion with slower release rate in bentonite beads in comparison to those of Kaolin[59]. Bentonite or its derivative activated by acid is used to prepare composite gels by their addition with carboxymethylcellulose (CMC) gel. The CMC/Bentonite hydrogels showed shrinkage in water, and also the authors present that dried gels showed water sorption below 120% of their own weight. Also, the sorption equilibrium is found to reach within 20-40 minutes. DSC analysis revealed water to be in bound state in swollen gels. Study is done on herbicide Metolachlor from formulated gels. Fickian diffusion dominates the release with relation to the limited and quick swelling properties of dried gels. Acid-activated Bentonite showed more pronounced slow release and time taken for the release of 50% Metolachlor was 158 hours for composite gel [60]. Various clay-Based NPK fertilizers are prepared through grinding. Kaolin and Bentonite are used as supporters. The release features of NPK are depicted through leaching experiments. The results reveal positive impacts for the Kaolin and Bentonite supported NPK fertilizers in comparison with the traditional ones. Also, Bentonite is superior to Kaolin, the major reason being the

presence of large expansion space in the interlayer of Bentonite, which locked NPK in its matrix, hence, preventing their loss. Bentonite supported NPK fertilizer, Clay-NPK showed enhanced slow release effects. It is found that the release rate is highest for N then K and lastly P. Hence, Bentonite based NPK fertilizers have a great scope and value for the production and implication of slow release fertilizer [61]. The development of a clay based nitrogen fertilizer is done using natural Attapulgite (APT) clay, Ethylcellulose (EC) film and Sodium carboxymethyl cellulose/hydroxyethyl cellulose (CMC/HEC) hydrogel and tested for structural and chemical properties by Boli Ni et al [62]. Ammonium chloride, ammonium sulphate and urea are taken as nitrogen substrates and their release profiles are studied in the soil. Also, a mathematical model is presented for the same for calculation of diffusion coefficient. Impact of product over the soil water-holding and soil water retention is also checked, and the formulation is found to be efficient in reducing the nutrient loss and improving the water use efficiency. Another feature presented by the product is reduction in prolonged irrigation cycles, which would benefit in drought-prone conditions.

Shen YA-Zhen et al., proposed the development of a model membrane made fertilizer coated with polymer via three coating materials of silicones-acrylate emulsions (GA-1710, SD-528, SD-5281), via chemical modifications by reacted layer technology. The study focused over the potential of model membrane in diffusing nutrients, which aided in development of urea coated with polymer. Mid-infrared photoacoustic spectroscopy reveal that the cross-linker in silicones-acrylate emulsions after chemical modifications showed highly advanced properties of film-forming and urea diffusion. This is a major step ahead in the arena of polymer coated fertilizers, as different silicones-acrylate emulsions showed different style of urea release. Inferences for different samples: GA1710 and SD528- Good slow nutrient release for urea with 30 days release time in static water; SD521 showed poor slow release effect and presented a scope for chemical modification. Hence, silicones-acrylate emulsions, which were water borne, presented an enhanced application for development of water-based polymer coated fertilizers in combination with reacted layer technology [63]. Also, in comparison to non-coated fertilizer, polymer coated fertilizers present the slow release of nutrients. Subbarao et al. formulated the inferences based on their experimental study on water soluble Potash coated with polymer in the form of cylindrical pellet [64]. The authors present an in-depth study on varied variables viz. Quantity of fertilizer, replenishment time and the quantity of water surrounding the pellet. Potash and wet clay are mixed in known quantity to formulate pellets which are prepared using a cylindrical mold. The pellets are then coated with tooth paste containing calcium which also acts as a secondary nutrient for the soil, and also establishes proper adherence of polyacrylamide polymer over the pellet surface. Finally, the pellet is dipped in the polymer solution. The authors studied the same procedure by varying the quantities of potash and clay. Thus, lowering the quantity of water and potash both lowers the release rate.

Focusing on reducing the hazardous environmental impacts of applied fertilizers and also on increasing their plant uptake from the soil, an all new fertilizer is formulated which also exhibits water retention. For the purpose, poly (dimethylourea phosphate) is designed as a macromolecular fertilizer with less solubility in water prepared using N, N'-dimethylourea (DMU) and potassium dihydrogen phosphate. Wheat straw (WS), acrylic acid (AA), 2-acryloamino-2-methyl-1-propanesulphonic acid (AMPS) and N-hydroxymethylacrylamide (NHMAAm) are used for coating which aid in forming environmentally non-hazardous superabsorbent composite. Degradation studies of product in soil and also the affect of N-hydroxymethyl acrylamide on its degradation reveal promising results for its use in eco-friendly agro-applications [65]. The agro-productivity has seen a considerable increase in the recent years due to the improvisations done for the usage of fertilizers, which focus mainly on increasing the nutrient uptake by the plants from the applied fertilizers. The authors here focus on the development of Enhance Efficiency Fertilizers (EEFs) [66] with their use as

controlled release fertilizers and also as nitrification/urease inhibitors. The paper is centred over the process for enhanced efficiency fertilizer formulation and also their release patterns.

3. FERTILIZER NANOCOMPOSITES FOR CONTROLLED RELEASE

3.1. Need of Polymer Fertilizer Nanocomposites

Nanoparticles are molecules depicting at least one of their dimensions in the nanoscale range, usually less than a few hundred nanometers. This reduction in size of the particles brings about most prominent changes in their properties owing to the exposure of large surface area for interaction during various reactions. And so, nanocomposites have emerged as most promising class of modified particles being highly attractive because of their biodegradable and hydrophilic nature which is being exploited in a lot of applications [67]. Also, the conventionally coated granules of fertilizers contain a small amount of active material coated with a polymer or other substances due to which, the amount of total needful nutrient or active content which comes in contact with the soil and thereby to plant gets reduced significantly. The aforesaid limitation led to the formulation of nanocomposites, which offer a large area of active component to be in contact with plant, and hence help in better and controlled release characters of the nutrients [68]. Apart from this, nanocomposites are also known to provide protection to plant against pests or pathogens, keep the soil structure intact, and also help curb plant related diseases [69].

3.2. Overview of Polymer Based Fertilizer Nanocomposites

Being the most important nutrient source in agri-production, nitrogen is the key player in enhancing the production quality and quantity both. But more than 100nm particle size dimension applied nitrogen encounters around 50-70% of losses to the environment due to leaching. Nilwala Kottegoda et al. stated that the advances in up surging nanostrategies have benefited to improve the Nitrogen Utilization Efficiency (NUE) to high efficacy of nano-fertilizer owing to their high surface area-to-volume ratio. The authors also propose a methodology for controlled nitrogen release by encapsulating urea-modified hydroxyapetite nanoparticles into Gliricidia sepium cavities. The study of release is done over three types of soil with varying pH with subsequent comparison to traditional fertilizers available commercially. The inferences show that nanofertilizers show a controlled release even on day 60[70]. In their extensive review Lav R. Khot et al., brought into light the positive impacts of highly advanced formulations of nanomaterials into varied shapes and sizes which are of great importance as they open up new avenues of research for the induction of newfangled characteristics into them, which aim at specific targeted implications. As a matter of fact nanomaterials have made their place in varied fields from medicine to food processing, but the use of same in agronomics is still incomplete. Exploiting the very fact, the authors present the fundamental observations, which reveal the use of nanomaterials in enhancement of seed germination and growth. They also aid in protection of plant by detection of pathogen and pesticide/herbicide residue. The review states the applicability of nanomaterials in the field of agriculture with focus on their future scopes [71]. The diverse available forms of nanomaterials are used in variety of fields as additives or even as active ingredients to enhance the product efficacies. But, there is still a greater need to establish the acceptance of nanomaterials, commercially.

The formulation of organic-inorganic nanohybrid material with its ion exchange capacity for the synthesis of 2, 4-dichlorophenoxyacetate (24D) which acts as herbicide is also taken into consideration [72]. The authors used the self-assembly technique wherein, inorganic Zn-Al layered double hydroxide (ZAL) acted as a matrix and 24D as the active agent. The release behaviour of 24D relied upon the type of anions and also their concentrations in the aqueous solution.

These factors are responsible for the initial rapid release of 24D, which became controlled gradually. The authors also propose the possible mechanism for the controlled release of intercalated 24D into Zn-Al-LDH (Layered double hydroxide) inorganic lamella (ZAD) from CR formulation with the focus on a futuristic approach that, 24D possess herbicidal properties; its controlled release from nanocomposites can be used to prepare a CRF of herbicide. Further, the development of a nanopesticide for agricultural applications as a potential tool is forethought. So far, the work done in the field of agriculture using Nanotechnical materials lacks information about nanopesticides and their efficiency. Henceforth, the very fact became a motivation for eco-friendly and cost effective nanopesticides [73]. The necessity of devising empirical methods for their development, based on bioavailability taking into account the environmental risk factors is also stated. Also, an extensive review focusing on the prime requirement of precision in farming to curb the food demands of the surplus population in the arena of decreasing lands and ever expanding human civilization, and covering the usage and importance of nanomaterials in agriculture sector as in nano-carriers for delivering fertilizers, nanopesticides, nanoherbicides and also food packaging is presented [75]. An intricate study on the inclusion of nanoparticles in 3D-polymeric structures for preparing novel multicomponent systems with varied functions in a hydrogel network which is a hybrid is presented. Though the focus is on formulating a controlled release drug delivery system, yet the technology can be experimented for the preparation of hybrid hydrogels for use in agriculture [75]. A variety of Nanoparticles those of inorganic/ceramic like silica, silicates, calcium, phosphate, polymeric nanoparticle etc. were used to formulate reinforced polymeric hydrogels by combining them with polymeric networks. Conclusively, the incorporation of nanoparticles in hydrogels provided new functionalities along with the enhancement of existing ones.

Certain nano-subnanocomposites are prepared using natural Kaolin and abandoned foam plastics for the purpose of selecting cementing and coating materials for slow/controlled release fertilizer. Methods used: organic material intercalation, cut at high velocity techniques, semi emulsification. Intercalation of organic materials is done into the Kaolin clay layers which then exfoliated to layers of nano-size through hydrogen bond formation [76]. Kabiri et al., highlighted the versatility of superabsorbent hydrogel composites (SHCs) and superabsorbent hydrogel Nanocomposites (SHNCs) which are formulated by addition of organo-modified clays to superabsorbent in order to increase their domain of use as in agriculture like soil conditions and controlled nutrient release or in bio-related use, fibers/textiles etc. The novel superabsorbent hydrogels are cost effective and present efficient mechanical properties [77]. A newfangled hydrogel series with polyacrylamide (PAAm), methylcellulose (MC) and calcic montmorillonite (MMt) achieving controlled release along with higher loading of fertilizer is also highlighted [78]. Characterization of hydrogel formulation is done on varied factors like thermal, kinetic and morphological properties and structural and spectroscopic examinations. The efficiency of the nitrogen fertilizer, urea is verified by using sorption and desorption studies. The inferences from the study showed the supremacy of hydrogel nanocomposites in adsorbing urea through the process of hydrolysis, and hence posing an increment in load content in accordance with the increment in mass of the clay. Clay got incorporated in the hydrogel polymeric matrix as revealed by FT-IR, which subsequently elevated the speed of absorption of water. Intercalation and exfoliation of clay in the matrix is showed by XRD. The authors concluded in their study that, because of montmorillonite in the hydrogel, the release of nutrients occurred in a much controlled manner than from pure hydrogel formulations at varied pH ranges. Conclusively controlled urea desorption gave best results showing the presence of 50% calcic montmorillonite in the hydrolyzed hydrogels with larger nutrient release efficacy at a speed 200 times controlled than urea without hydrogel and proving the potentiality of the system for use in agriculture sector.

The technique of in-situ polymerization is used for polymerization of sodium alginate, acrylic acid, acrylamide

and montmorillonite with plant nutrients, in order to obtain an all new NPK fertilizer depicting slow release properties and also encapsulating the same by superabsorbent nanocomposite. FT-IR, XRD and SEM were used to generate data regarding grafting, structure and interactions of nanocomposites. The inferences after taking in account the studies pertaining to release of fertilizer showed that montmorillonite is the effective component in context to the controlled release of nutrients in comparison to superabsorbent only. Overall results indicated the superiority of the preparation with the said components, with respect to better water retention capability and also slow release mechanism [79]. Pollution of environment due to nitrogen has become a major concern since the evolution of various classes of fertilizers. A novel slow released NPK fertilizer encapsulated by superabsorbent nanocomposite is prepared via in-situ free radical polymerization of sodium alginate, acrylic acid, acrylamide, and montmorillonite in the presence of fertilizer compounds. Evidence of grafting and component interactions, superabsorbent nanocomposite structure and morphology is obtained by a FT-IR, XRD and SEM techniques. The water absorbency behaviour of superabsorbent nanocomposite is investigated. After those characterizations, the potential application is verified through the study of fertilizer release from prepared formulations. Results indicated that the presence of the montmorillonite caused the system to liberate the nutrient in a more controlled manner than that with the neat superabsorbent. The good slow release fertilizer property as well as good water retention capacity showed that this formulation is potentially viable for application in agriculture as a fertilizer carrier vehicle [80]. Montmorillonite is exfoliated in the matrix in the urea/urea formaldehyde polymer to prepare a new nanocomposite for using it as a nitrogen-loaded slow release fertilizer. The nanocomposites are formulated using the simple and highly productive cold plastic extrusion method through formaldehyde, which was added as a precursor for achieving in situ polymerization simultaneously with the extrusion process. The inferences after the characterizations of the nanocomposites revealed positive results after extrusion in context to the slow release of urea, and also showed enhanced mechanical resistance. Nanocomposite structure also showed enhanced slow release behaviour in the immersion tests done in water. The study concluded urea-formaldehyde polymer nanocomposites to be efficient components for improving the efficiency of nitrogen release from fertilizers and also the utilization of the same by plants [81].

Pollution of environment due to nitrogen has become a major concern since the evolution of various classes of fertilizers. The authors herewith focused on minimizing the same by enhancing the utility of fertilizers by developing an all new palygorskite (PGS) nanocomposite adsorbent, which is then utilized for recovery and reuse of NH_4^+ in agricultural practices found in wastewaters containing ammonium in the form of a multifunctional slow-release ammonium fertilizer (MSAF). The results are in accordance with the desired factors like removal of ammonium and highly efficient slow-release with a wide pH range of 4.0 to 8.0. Study is done at various operational conditions where pseudo-second-order kinetic model and Freundlich model provided the kinetic data which indicated that equilibrium due to adsorption was achieved within 12 minutes with wide adsorption capacity of 237.6mg g-1 even when PGS was used as nanofiller by 30 wt%. The use of composite material proved to be beneficial as it was efficient even in keeping the soil moisture content intact owing to its better water absorbing and retention capacities which proved to be promising in the long run of modern agriculture and horticulture [82]. Liang et al., worked over increasing the temperature range of Nanocomposites and prepared a thermosensitive polymer-clay Nanocomposite using clay-poly(N-isopropylacrylamide) (PNIPAAm). Nanocomposites are organically modified. Product shows better thermal transition efficiency and also speedy transition kinetics. XRD characterization reveals the partial intercalation and particle exfoliation of clay minerals of Nanocomposites in dried state, but majorly exfoliation when swollen. The variation obtained from the use of different Nanocomposites opens up to an all new scope to coincide the thermal transition by managing the polymer-nanophase material

interactions[83].

Bhupinder Singh Sekhon posted an elaborated review describing Nanotechnology as a pivotal tool for the improvisation of certain methodologies in the field of Agriculture and strives for rigorous futuristic economic growth. Agri-products encase crops for human consumption as well as animal feed, and hence thrive for sustainability and protection of the same. The author herewith, opens up large domains where nanotechnology aids in the agri-production viz., improving fertilizers; setting up nanosensors for plant protection; developing nanodevices for genetic manipulation of plants and also diagnosing diseases in them; and also managing animal breeding and health along with proper management of post harvest. The paper stated the benefits of using nanomaterials in the arena of agriculture, as it can benefit the farmers by minimizing the losses of applied nutrients through fertilizers by reducing leaching and emissions, which would in turn be better for the soil in the long run. Making the workers and consumers both aware for nanoscience can enhance the biomass-to-fuels production system, and can reduce the ill effects on environment due to the traditional practices in farming [84].

Taking into account the biodegradability and non-toxic antibacterial properties of Chitosan derived from Chitin, Khalil et al., have presented a deep study on the same by blending it with cellulose derived nano-fibre in order to enhance its mechanical and thermal properties. The results show wide applicability of Chitosan based composites derived from nano-cellulosic fibres which act as attractive reinforcement in chitosan and provide eco-friendly, physically efficient composite films[85]. Amanda S. Giroto et al., centered their research on improving the fertilization practices in crop production with a quest to add-up to the globally shooted food demand. The approach highlighted by the author kept the enhancement of interaction between phosphate and urea via nanocomposites as the focal point which also benefited in controlling the release of these nutrients in the soil. Urea(ur) or extruded thermoplastic starch/urea (TPSUr) blends were used as a matrix to prepare the nanocomposites. Hydroxyapatite (Hap) particles were dispersed in the matrix in a ratio of 50% and 20% Hap. To examine the effect of nanocomposites over nitrogen and phosphate availability in the soil, two incubation experiments and release tests were conducted and it was found that there does existed an interaction between morphological changes in nanocomposites and the components of the fertilizers. In addition to providing controlled release of urea, TPSUr nanocomposites also lowered NH3 volatilization. They also showed an increment in release rate of phosphate in citric acid solution. Presence of Hap in dispersed form in matrix of urea posited a decrement on phosphate adsorption, hence making it available even after four weeks of soil incubation [86].

The environment suffers negative effects coz of liberation of ammonia as an aftermath of application of urea as a fertilizer in soil. The effectiveness of coated urea granules still suffers a backlog as it requires a high degree of interaction between the coating and the subsequent nutrient core. An all new approach of exfoliation of clay over urea matrices is adopted to prepare fertilizer Nanocomposites with or without polymerization. Interaction between additives and the major nutrient supplier, urea is enhanced by formaldehyde. The trial for same is carried out on ryegrass in greenhouse where the study is done comparing various slow release formulations for fertilizers on the grounds of ammonia released and the efficiency of nitrogen uptake from urea. Various deciding factors for the slow release behaviour of urea nitrogen in the soil include the thickness of composites, their solubility and also the chemical formulation.

Table 2. Different Formulations of MMT Clay and Urea Percentage Used

Name	% of MMT	% of Urea
MU 1:4	20	80
MUHG 1:4/2 (with 1.96% polyacrylamide hydrogel)	19.6	78.4
MUPf 1:4/0.5 (with para-formaldehyde in 0.5 molar ratio)	20	80
MUPf 1:1/0.5 (with para-formaldehyde in 0.5 molar ratio)	50	50
MUPf 1:1/1 (with para-formaldehyde in 1 molar ratio)	50	50

It is concluded from the study that ammonia volatilization is greatly reduced because of use of nanocomposites of urea, which is a result of slow release of urea nitrogen in the soil. Consequently, the plant nutrient demand is fulfilled gradually as desired [87].

The degradation of environment through agrochemicals is largely done by urea which is hydrolyzed by urease. This also results in low utilization of the same by the plant. In order to fight the very issue, a novel nanocomposite is formulated as a fertilizer synergist (FS) via sodium humate-attapulgite-polyacrylamide. This FS is found to pose some positive impacts like lower loss of nutrients, better uptake by plants, and improved organic matter of soil, and also enhanced the gene expression related to nitrogen uptake. The novel formulation also increase the number of nitrogen metabolizing bacteria, thereby modifying the soil-microbiota which also led to better degradation of organic matter in the soil. Hence, it has proved to be one of the best contenders which can monitor the major nutrient required by the plants, i.e. Nitrogen, hence aid in development of agriculture as a whole [88]. Efficacious utilization of nitrogen provided to the plants is the key factor to the production rate in agriculture. Contributing to the same, Pereira et al., formulated a study which explained the effect on release rate of urea and structure. They also focused on the workability of nanocomposites of urea when exfoliated with a clay-based mineral synthesized by the combination of hydrophilic or hydrophobic polymers in different concentrations. High nutrient load of nanocomposites, nearly 75% itself acts as the structural matrix for the same. The paper also presents an economic method of plastic mixture extrusion for scaled up granule production. Polyacrylamide hydrogel and polycaprolactone were used to prepare nanocomposites, which reduced the emission of nitrous oxide (N_2O) up to substantial levels [89]. Past decades have seen stagnancy in the nutrient utilization by plants for N, P and K through conventional fertilizers. To overcome the scenario, nanotechnology with its distinct beneficial characters has been used to synthesize nanofertilizers singly by nutrients, or even in combination with adsorbents of nano-dimension. The most important feature of nano-fertilizers is their potential to slowly release the fertilizer, thereby reducing the loss of nutrients and also keeping the environmental safety intact [90].

Agriculture is facing the challenge to provide food security for a growing world population without impacting environmental security. It is necessary to use modern technologies in agroecosystems A combination of biotechnology and nanotechnology has the potential to revolutionize agricultural systems and provide solutions for current and future problems. These include the development and use of smart fertilizers with controlled nutrient release, together with bioformulations based on bacteria or enzymes [91].

3. CONCLUSIONS AND FUTURE SCOPE

The evolution of traditional Nitrogen based fertilizers has seen a steep improvement from being converted into controlled release fertilizers or CRFs to the latest and all new formulations done with the extensive support of Nanotechnology. Nanotechnology in agriculture has promising scope in the development of the same, which could lead

agro-based economies to newer heights. Nanoparticle production is comparatively easier and has the great potential in controlled release of certain nutrients providing a larger surface area for release simultaneously. They can also aid largely in the macronutrient targeted delivery, which is require for the enhancement of plant resistance and defence mechanism against certain diseases. Apart from this, the plants can also improve plant properties through genetic modification. One of the major advantages presented by nanoparticle formulation is that, it provides a wide scope for the usage of biodegradable binding materials like clays unlike CRFs.

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