धान एवं गेहूं की फसलों में नाइट्रोजन उपयोग/रिहाई के लिए नैनाक्ले पॉलीमर कम्पोजिट के साथ बायोडिग्रेडेबल पॉलीमर का प्रयोग

Nanoclay Polymer Composites (NCPCs) with biodegradable polymers for controlled release of nitrogen in rice and wheat crops

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Nanoclay Polymer Composites (NCPCs) with biodegradable polymers for controlled release of nitrogen in rice and wheat crops

By

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CERTIFICATE

This is to certify that the thesis entitled "**Nanoclay Polymer Composites (NCPCs) with biodegradable polymers for controlled release of nitrogen in rice and wheat crops**" submitted to the Faculty of the Post-Graduate School, Indian Agricultural Research Institute, New Delhi, in partial fulfillment of the requirements for the degree of **Doctor of Philosophy in Soil Science and Agricultural Chemistry,**, embodies the results of *bonafide* research work carried out by **Ms. Kirti Saurabh**, under my guidance and supervision, and that no part of this thesis has been submitted for any other degree or diploma.

It is further certified that any assistance and help availed during the course of investigation as well as source of information have been duly acknowledged by her.

Place: New Delhi **(K. M. Manjaiah)**
Date: ***Chairman***
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Place: New Delhi

Dated: (Kirti Saurabh)

Dedicated to

My Family

&

Manjaiah sir

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1. Introduction

Nitrogen (N), the most vital element for plant development, so required in large amounts and should be added to the soil to avoid a deficiency. Among the N fertilizers, in South East Asia the most usually utilized is urea on account of its high N content and relatively low cost. However, around 40–70% of N from the applied fertilizers is lost to the environment which causes huge economic and resource loss as well as results in intense serious environmental pollution. The environmental pollution is principally because of high dissolvability and volatility of urea which is responsible for high surface run off with rain or irrigation water, leaching and vaporization. In this way, it has made tremendous keenness among the researchers to develop new innovation that would beat the constraints of applying urea.

Since the early 1970's, keeping in mind the end goal to beat the limitations of urea in agricultural use, scientists are attempting to prepare slow/control-release fertilizers. The motivation behind the vast majority of these works is to enhance the utilization of fertilizer and water resource at the same time, and decrease the contamination brought on by imbalanced fertilization, several nanoclay composites based superabsorbent slow release fertilizers are specified in literature. In agriculture superabsorbent polymers are utilized as a soil additive, as reservoir of nutrients, and as water superabsorbent in the soil.

Superabsorbent polymer nanocomposite fertilizers are the technologically most advanced enhanced efficiency fertilizers. A number of natural and synthetic polymers have been studied and used in controlled release formulations for different agricultural nutrients. Natural polymers such as starch (Jin *et al.*, 2013; Otey *et al.*, 1984; Xie *et al*., 2008), cellulose (Dubey *et al.*, 2011 & Ni *et al.*, 2011), lignin (Li & Wang, 2012; Park *et al.*, 2008 & Fernández-Pérez *et al.*, 2008), chitosan (Hussain *et al.*, 2012; Jamnongkan & Kaewpirom, 2010), alginate (Wang *et al.*, 2012; Connick, 1983), wheat gluten (Castro-Enríquez, 2012), rubber (Hassan *et al.*, 1992; Hepburn & Arizal, 1988) and latex (Yao *et al.*, 2005) in their natural or modified form have been investigated for their suitability in enhancing the efficiency of different fertiliser formulations. Various slow and controlled release fertilisers have been prepared using synthetic polymers such as polyolefines (Xu *et al.*, 2013), polyurethane (Ni *et al*., 2011), polyacrylic (Liang *et al*., 2007), polyacrylamide (Rahman *et al*., 2008), polysulfonate (Tomaszewska & Jarosiewicz, 2006), polyvinyl chloride (Hanafi *et al*., 2000), polystyrene (Liang & Liu, 2006), polylactide (Xie *et al*., 2008), polyacetate (Niu & Li, 2012), and polydopamine (Jia *et al*., 2013). Though these polymers have great significance as slow release fertilizer carrier, the high cost of such products in the market ends up making its application impractical. Therefore, to enhance the fertilizer performance and to reduce the cost, many researchers had used naturally available inorganic clays such as montmorillonite and hectorite (Marandi *et al*., 2015), rectorite (Wang & Wang, 2009), attapulgite (Deng *et al*., 2012), kaolin (Hussien *et al*., 2012), clinoptilolite (Rashidzadeh *et al*., 2014) and bentonite (Shirsath *et al*., 2011) in variable proportions. Moreover, it has been proved that the inclusion of inorganic clays into composites decreases the release rate of fertilizer from a slow release formulation (Liang and Liu, 2006).

Several agronomic studies have revealed that superabsorbent nanocomposite fertilizers are superior to conventional fertilizers. Sarkar and Datta (2014) prepared fertilizer loaded nanoclay superabsorbent polymer composite (NCPC) by taking acrylic acid and acryl amide monomers. They reported that addition of NCPC-H (high dose) and NCPC-L (lower dose) resulted in 18% and 26% additional biomass yield of pearl millet over conventional fertilizer higher and lower dose, respectively. Islam *et al.* (2011) used the reduced rate of chemical fertilizer along with water-saving superabsorbent polymer (SAP) for field crop production. The objective was to evaluate the effectiveness of different rates of SAP (low, 0.75; medium, 11.3 and high, 15.0 kg ha^{-1}) against half amount of conventional standard rate of chemical fertilizer for summer corn (*Zea mays* L.) production in a drought-affected field of northern China. Corn yield increased following SAP application by 11.2% under low, 18.8% under medium and 29.2% under high rate with only half amount (150 kg ha^{-1}) of fertilizer compared with control plots, which received conventional standard fertilizer rate (300 kg ha^{-1}). Rahman *et al*., (2008) prepared slow release N-fertilizer consisting of acrylamide (AAm) and maleic acid (MA), abbreviated as P (AAm-MA) and investigated the growth and yield from green chilli (*Capsicum annuum)* after applying this. The results suggested that P (AAm-MA) improved the growth of plants as well as sustained higher N level in soil for longer time due to the reduced surface runoff, evaporation and leaching. Zvomuya *et al.* (2003) reported that at 280 kg ha^{-1} N, NO_3-N leaching was 34 to 49% lower with Polymer Coated Urea (PCU) treatments than three split applications of urea while nitrogen recovery efficiency (RE) for PCU averaged 50%, 7% higher than urea (43%). A creative design from Wu *et al.*, (2008) involved a double-coated slow release NPK compound fertilizer with superabsorbent and water-retention. The material was coated by crosslinked poly (acrylic acid)/diatomite–containing urea composite (PAADU), chitosan and water-soluble granular fertilizer NPK. It was found that this product can adsorb water about 75 times its own weight if it swelled in tap water at room temperature for two hours. In addition, the mixture of PAA and NPK compound fertilizer had a slower release rate than untreated NPK. Poly acrylamide/methyl cellulose/montmorillonite nanocomposite hydrogel has been utilized for slow release of urea (Bortolin *et al.*, 2013)

Although synthetic polymers possess better mechanical and control release properties, the accumulation of residual or undegraded synthetic polymers in the soil may create a new type of pollution. Polymer used in slow release fertilizers may leave undesired residues of synthetic material on the fields. Some types of polymers used in the coating of conventional fertilizers currently in use decompose extremely slowly in the soil. Their use may thus lead to an undesirable accumulation of plastic residues. Therefore, natural polymers are preferred over the synthetic polymers because of their non-toxicity, water solubility and biodegradability. However, higher cost and poor control over nutrient release are limiting factors. Therefore, current research focus regarding the use of biodegradable polymers as coating materials is directed towards reducing the cost of production and better control of nutrient release. The applications of wheat straw (Liang *et al.*, 2009; Xie *et al.*, 2011) and similar lignocellulosic residues and clay materials (Ni *et al.*, 2010) have also been explored for producing controlled release fertilisers.

Development of using biodegradable superabsorbent hydrogels to reduce crises such as nutrient loss, soil erosion, frequent droughts or providing food security requires knowledge of their behavior and performances in the soil. With regard to importance of using super-absorbents, it is necessary to carry out research on effects of different types of super absorbents; comparison of their degradability; quantities and methods of their use for different plant species under different climatic and soil textures. Keeping this in view, the present study has been planned with the following objectives:

Objectives

1. Synthesis and characterization of NCPCs with biodegradable polymers.
2. To study degradation behavior of NCPCs under different soil environments.
3. To evaluate the above NCPCs with respect to N use efficiency in crops and N dynamics and biological properties in soil.

To accomplish the above objectives, two independent approaches were employed. In the first approach, a series of nanoclay-polymer composites were synthesized by using acrylic acid, acryl amide, sodium alginate and wheat flour. Subsequently, the NCPCs were characterized by FTIR, XRD, SEM, SEM-EDX, TEM and water absorbing capacity was determined. Further, release of N in water and soil, and degradation behavior study were also carried out.

For achieving the third objective, a greenhouse experiment was carried out to study the effectiveness of the synthesized nanoclay-polymer composite (NCPCs) in terms of N release, N_2O emission, its effect on soil biological properties like MBC, MBN, dehydrogenase, phosphatase and urease activity.

2. Review of Literature

The pertinent literature on the study of '**Nanoclay Polymer Composites with biodegradable polymers for controlled release of nitrogen in rice and wheat crops**' was reviewed under the following heads:

2.1. Synthesis of biodegradable nanoclay-polymer composites (NCPCS) and subsequent loading with urea

Fertilizer is one of the indispensable input materials for the crop production and is major component of cost of cultivation and pollution. However, more than half of the applied amount of common fertilizers cannot reach the plant, but it is washed off by rain and irrigation water (Bajpai and Giri, 2002; Guo *et al.*, 2005). This portion of lost fertilizer causes vast financial misfortunes as well as intense environmental contamination. The overcoming of these inadequacies can be accomplished with the utilization of slow release fertilizers (SRFs). SRFs are intended to gradually discharge fertilizers to plants at a rate toharmonize with the nutrient requirement of a plant, while simultaneously reducing fertilizer loss (Liang and Liu, 2006; Teodorescu *et al.*, 2009). As water is considered one of the main factors that limit the production of agriculture, so the use of water resource should be done very efficiently. Recently, investigation on the use of superabsorbent as water management materials for agricultural applications has attracted great attention. Superabsorbent polymers are cross linked hydrophilic polymers that can absorb water, saline solutions, or other liquids up to hundreds of times of their own weight (Seetapan *et al.*, 2011). In farming uses, particularly in dry zones, the utilization of superabsorbents leads to increase the water-holding limit and thus the fertility of the soil (Zohuriaan-Mehr *et al.*, 2010). From the application perspective, the blend of superabsorbents and SRFs might enhance the water-holding capacity and nutrient retention of sandy soils furthermore increase the soil's aeration and microbial action, and alleviate in the meantime the environmental impact from water-soluble fertilizers and lower frequency of irrigation (El-Rehim *et al.*, 2004). Mainly the superabsorbents are produced using synthetic hydrophilic polymers, for example, poly (acrylic acid) or its copolymer with poly (acrylamide) (Ni *et al.*, 2010). Though, the use of such synthetic polymers results in their accumulation over time because of poor degradability in soil, therefore the demand for using environmentally safe, degradable superabsorbent is continuously increasing. Whereas the demand for using natural hydrogels such as starch (Zhong *et al.*, 2013; Pourjavadi *et al.*, 2010 and Zhang *et al.*, 2006), cellulose (Bao*et al.*, 2011; Chang, *et al.*, 2010), chitosan (Jamnongkan and Kaewpirom, 2010; Zhang *et al.*, 2007), and alginate (Sadeghi *et al.*, 2014; Rashidzadeh and Olad, 2014; Liu *et al.*, 2008) as fertilizer carriers, due to their biodegradability and low costs, is continuously increasing. Biopolymers like starch and alginate, being renewable and eco-friendly biodegradable materials are gaining considerable importance in agriculture to be used as a fertilizer carrier (Jin *et al.*, 2013; Ni *et al.*, 2010; AbdEl-Rehimand Hassan, 2006).

Several reports have shown a decrease in grain yield under water deficit due to reduces leaf photosynthesis and thus reduce the thousand grain weight (Engel, 2003; Emam, 2007). Use of some materials such as superabsorbent polymers in soil, increases water retention in the soil and thus reduce the consumption of water and fertilizers leaching. These materials can reduce the effects of water stress on the plant and lead to increased yield in arid and semiarid regions (Widiastuti *et al.*, 2008). The amount of water absorption in these polymers, depending on the formulation, water, impurities and the amount of salt contained is variable up to 400 times the weight of the superabsorbent (Monnig, 2005). Superabsorbent polymers increases water retention in the soil and reduced irrigation number to 50% (Nazarli *et al.*, 2007). In some situations, super absorbent polymers are used as releasing fertilizer agent of soil matrix, so that the polymerabsorbs the nutrients needed by the plants and releases them gradually for the plants and thus prevent leaching of these elements. He *et al.* (2007) reported that the nutrient release of water-absorbent slow release nitrogen fertilizer (WASRNF) is much slower than that of urea during the 15 days of release study.

Although of the above mentioned advantages still one disadvantage is associated with these fertilizers, that the most polymers used are not biodegradable and accumulate in the soil causing many environmental problems. Polymer used in slow release fertilizers may leave undesired residues of synthetic material on the fields. Some types of polymers used in the coating of conventional fertilizers currently in use decompose extremely slowly or not at all in the soil. Their use may thus lead to an undesirable accumulation of plastic residues. Further, if the polymer

Bahrami and Mahdavinia, 2016	Nanocomposite hydrogels based on *kappa*-carrageenan incorporated with sodium montmorillonite (Cloisite) nanoclay	Pristine Na-MMt showed a diffractive peak at $2\theta=7.6$ corresponding to the distance of clay sheets with d spacing 11.61 Aº. No diffraction peak was observed in nanocomposite and it can be concluded that the clay layers are completely or partially exfoliated.	The characteristic vibration bands of the clay (-OH stretch from lattice hydroxyl, -OH stretch fr om free H2O, -OH bending and Si-O stretch) are shown at 3633, 3447, 1641 and 1043 cm-1, respectively. bands observed at 840, 922, 1026, and 1229 cm^{-1} were attributed to D-galactose-4-sulfate, 3,6 anhydro-D-galactose, glycosidic linkage, and ester sulfate stretching of carrageenan, respectively. The broad band at 3200–3400 cm^{-1} is due to stretching of -OH groups of carrageenan.		The dark and thin lines corresponded to Na-MMt layers. It can be seen that Na-MMt layers were obtained and indicates that the clay layers exists in exfoliated type.
Rashidzadeh and Olad, 2014	NPK fertilizer encapsulated by superabsorbent nanocomposite of sodium alginate, acrylic acid, acrylamide, and montmorillonite	The crystalline peak of MMT is observed at about 7.33 corresponds to the periodicity in the direction of (0 0 1) of the MMT In the case of Hyd/MMT, the (0 0 1) peak is shifted toward a lower angle (7.15˚). This results from	Montmorillonite: the strong absorption peaks at 1029 cm^{-1} (Si-O bond stretching), 522 cm^{-1} (Al-O bond stretching) and 462 cm^{-1}(Mg-O bond stretching) are characteristic peaks of MMT Sodium alginate: around 1640 cm^{-1} and 1419 cm^{-1} wave numbers (carboxylate	A homogeneous, high porous with honeycomb-like structure with pore sizes in the range of several tens of microns was clearly shown for Hyd sample. Hyd/MMT:	

'shell' fragments do not compose, the fragments, which are smaller than sand size particles, become part of the soil. At present, polymer's degradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues (Shavit *et al.*, 2002). Thus, it is the common consensus that non-biodegradable waste has to be avoided, and biodegradable products have to be fully-utilized as much as possible under reasonable economic and ecological conditions in order to build a friendly environment that can lead sustainable development for a country.

Even if biodegradability has become a highly subjective matter nowadays, the perceptions about the biodegradability of a polymer are being changed with everyday development of new biodegradable polymers from a variety of renewable natural resources. For example, nature-inspired synthetic polydopamine (Pdop), and synthetic polylactic acid (PLA) and Poly(3-hydroxybutyrate) (PHB) derived from renewable natural resources are now acceptable as biodegradable polymers with their applications in polymer coated controlled release fertilizers (Costa *et al.*, 2013;Jia *et al.*, 2013). ASTM standard D-548894d defines the term "biodegradation" for the materials "capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds or microbial biomass in which the predominant mechanism is the enzymatic action of microorganisms, which can be measured by standard tests, in a specified period of time, reflecting available disposal conditions". Figure 2.1 classifies those biodegradable polymers or blends that are reported for controlled release fertilizers based on either hydrogel or non-hydrogel properties.

To make these superabsorbent polymers more cost effective and to release nutrient efficiently now-a-days clay minerals like montmorillonite, rectorite, attapulgite, kaolin, and many others are incorporated into it. Polymer nanocomposites are hybrid organic–inorganic materials with at least one dimension of the filler phase less than 100 nm (Mittal, 2010). Polymer nanocomposites are synthesized via various methods that can be categorized into four major routes: melt intercalation, template synthesis, exfoliation adsorption, and in situ polymerization intercalation (Mittal, 2010; Ray and Okamoto, 2003; Pavlidou and Papaspyrides, 2008; Abedi and Abdouss, 2014; Mittal, 2009 & Alexandre and Dubois, 2000).

Intercalation in molten state: In this technique, developed by Vaia and Giannelis, 1997, the clay is mixed with a thermoplastic polymer matrix in its molten state, Figure 2.2. Under these conditions, the polymer is taken to the space between the layers forming a nanocomposite. The driving force in this process is the enthalpic contribution of the interactions between polymer and clay, which in this case fulfills the functions of the nanocharge. Melt intercalation is the typical standard approach for synthesizing thermoplastic polymer nanocomposites. It involves annealing the polymer matrix at high temperatures, adding the filler, and finally kneading the composite to achieve uniform distribution. It has the advantage of being environmental friendly because of the lack of solvent usage.

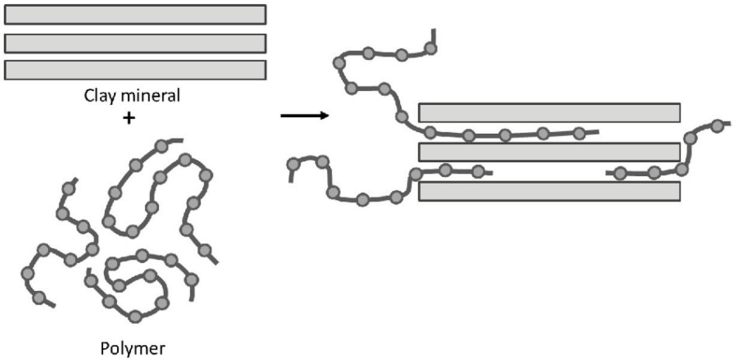

Figure 2.2 Nanocomposites synthesized by intercalation in molten state.

Dispersion in solution: In this method of synthesis, clay is exfoliatedin single layers using a solvent in which the polymer or prepolymer issoluble. The clay’s layers can be easily dispersed in the solvent throughthe increase of entropy due to the layers’ disorganization, which exceeds the laminates’ organizational entropy value. Afterwards, the polymeris embedded into the delaminated layers and when the solvent isevaporated or the mixture is precipitated, the layers merge with the polymer as filler, Figure 2.3.

This technique is especially employed with water-soluble polymers. For example, polyvinyl alcohol (PVA) used by Strawhecker and Manias (2000), poly(acrylic acid) employed by Billingham *et al.* (1997), andpoly(ethylene oxide) by Malwitz *et al.* (2003). That is due to the polarity of these polymers, which is believed to contribute an enthalpy gain helping intercalation. Therefore, the main requirement of this method is that the chosen polymer should be compatible with the chosen solvent. Remarkably, this method produces a high degree of intercalation onlyfor specific polymer/clay/solvent systems, suggesting that for a given polymer, one has to find the right clay, organic modifier and solvents.

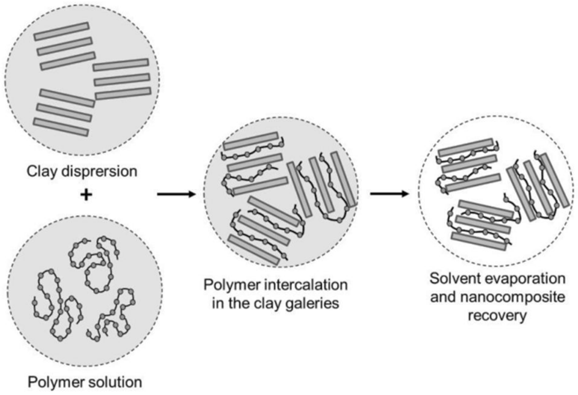

Figure 2.3 Synthesis of nanocomposites by dispersion in solution technique.

In situ polymerization intercalation: involves the swelling of the filler in liquid monomer or monomer solution as the low-molecular-weight monomer seeps in between the interlayers causing the swelling (Mittal, 2009). Polymerization starts using heat, radiation, initiator diffusion, or by organic initiator or catalyst fixed through cationic exchange (Alexandreand Dubois, 2000). The monomers then polymerize in between the interlayers forming intercalated or exfoliated nanocomposites (Figure 2.4). As an example, Baniasadi *et al.* (2010) used this method to obtain exfoliated polypropylene-based nanocomposites using a bi-supported catalyst. The advantage of this approach liesin the better exfoliation achieved compared to melt and exfoliation adsorption methods (Abedi and Abdouss, 2014).

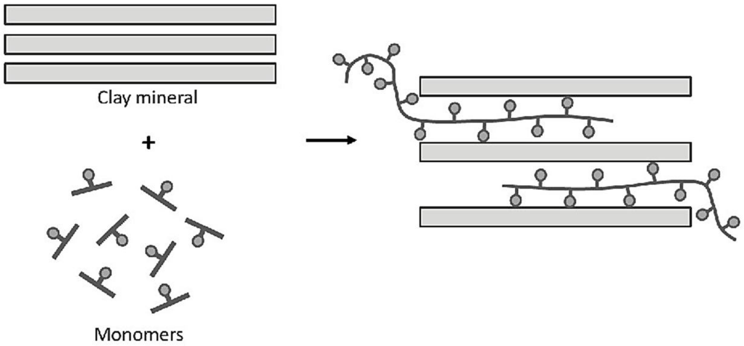

Figure 2.4 *in-situ* polymerization syntheses of Polymer-Clay Nanocomposites.

Template synthesis: also known as sol-gel technology is based on an opposite principle than the previous methods. This approach involves the formation of the inorganic filler in an aqueous solution or gel containing the polymer and the filler building blocks (Mittal, 2010; Pavlidou and Papaspyrides, 2008; Abedi and Abdouss, 2014; Mittal, 2009 & Alexandre and Dubois, 2000). The polymer serves as a nucleating agent and promotes the growth of the inorganic filler crystals. As those crystals grow, the polymer is trapped within the layers and thus forms the nanocomposite. It is mainly used for the synthesis of double-layer hydroxide-based nanocomposite and is much less developed for the synthesis of layered silicates. This is because of the high temperature used during synthesis that degrades the polymer and the resulting aggregation tendency of the growing inorganic crystals (Pavlidou and Papaspyrides, 2008; Mittal, 2009). Therefore, this processis not commonly used.

SAP hydrogels are synthesised from synthetic polymers without natural polymers that have AA as the main component. Kabiri *et al.* (2003) carried out their research regarding the effect of the concentration and type of crosslinker on the porosity and adsorption rate of highly porous SAP hydrogels formed from high concentration of AA/potassium acrylate aqueous solutions using N-MBA and 1,4-butanedioldiacrylate as crosslinkers. It was concluded that both crosslinkers showed same effects on water absorbency in distilled water and saline. The gelation time decreased with increasing concentration of the crosslinker especially N-MBA.

Liang *et al.* (2007) synthesized a SAP which possessed the core/shell structure which is urea formaldehyde (UF) and polyphosphate potassium, and the poly(acrylic acid-*co*-acrylamide)/kaolin respectively. The results showed that its water absorbency was up to 91 g/g in tap water. The SAP contained 11.3, 21.1 and 8.6 wt. % for N, P and K, respectively. The NPK nutrient release of the SAP was not above 75% on the 30th day and this concluded that it had a good slow release property in soil and water holding ability and water retention properties of the soil could be greatly improved. Availability of fertilizer and water resource to crops could be improved simultaneously.

Wu *et al.* (2008) prepared a double-coated slow-release NPK compound fertilizer with SAP using (acrylic acid)/diatomite (AA/DT) which contains urea, chitosan and water-soluble granular fertilizer NPK which were in the outer coating, the inner coating and the core respectively. The double coated SAP was undergone its swelling test and it was found that it could swell 75 times of its own weight at room temperature for 2 hour. Besides, the SAP contained 8.47% of potassium, 8.51% of phosphorus and 15.77% of nitrogen through AAS and elemental analysis. The results showed that the slow release ratio of the effective nutrient in it was not exceeding 75% on the 30th day. This can be concluded that chitosan and diatomite in the production of coating material can reduce the production cost and the technique is environmental-friendly. Its slow release property could be useful in agricultural and horticultural purposes.

Wang and Wang (2010) synthesized a pH-sensitive semi-interpenetrating network (semi-IPN) SAP composed of NaAlg-*g*-poly(sodium acrylate) (NaA) network and liner polyvinylpyrolidone (PVP) via free-radical solution polymerization. Ammonium persulphate and N-MBA were used as the initiator and crosslinker, respectively in this reaction. The authors concluded that the introduction of PVP and the formation of the semi-IPN structure improved the swelling capacity and rate of swelling of the hydrogel.

Zhong *et al*. (2012) synthesized an eco-friendly SAP using modified sugarcane bagasse/poly (acrylic acid) embedding phosphate rock (MSB/PAA/PHR) in order to improve the water-fertilizer (NPK) utilization ratio. The result showed that MSB/PAA/PHR had an excellent water absorption capacity which achieved 414 g/g in distilled water and 55 g/g in 0.9 wt. % of NaCl solution, a preferable sustained-release property and this could also mitigate the environmental contamination.

Zhong *et al*. (2013) synthesized an agricultural SAP based on sulfonated corn starch/poly (acrylic acid) embedding phosphate rock (SCS/PAA/PHR) due to the difficulty of utilization of plants since phosphate rock is abundant. The result showed that SCS/PAA/PHR possessed an excellent sustained-release property of plant nutrient and the SCS/PAA improved the release of phosphorus nutrient.

Liu and coworkers (2013) synthesized a chitin-based acrylate superabsorbent by grafting copolymerisation chitin and acrylic acid with APS and N-MBA as initiator and crosslinker, respectively in NaOH/urea solution without nitrogen protection. The authors revealed that chitin which possesses more hydrophilic group in the graft copolymerisation reaction, significantly enhanced the water absorption of the product. Acrylic acid was expected to simplify the procedures and reduce the water consumption whereas NaOH and urea play the role of solvent and reaction reagents. Thus, the final product exists as a hydrogel without excess reagent emissions, which is conductive to reducing the environmental pollution.

Ge and Wang (2014) prepared chitosan-acrylic acid SAPs through thermal reaction without or with N-MBA and potassium peroxydisulfate as crosslinker and radical initiator respectively, under air or nitrogen atmosphere. The authors concluded that SAPs were successfully synthesized by the thermal reaction without using radical and crosslinker in air at atmospheric pressure. The results also showed that the yield of thermal reaction in air was similar to reaction in nitrogen atmosphere (radical and crosslinker were used) and the thermal reaction without using crosslinker and initiator was suggested since both of them are harmful or toxic to human body and environment.

Hemvichian *et al.* (2014) synthesized a SAP by using radiation-induced grafting of acrylamide (AM) onto carboxymethyl cellulose (CMC) and this SAP was loaded with potassium nitrate (KNO_3) as an agrochemical model which has a highly potential of controlled release system. The results showed avery high swelling ratio of 190 g/g of dry SAP. However, the swelling ratio and control release rate of KNO_3increased with decreasing of AM and irradiation dose.

By using an ionically crosslinked carboxymethyl cellulose hydrogel matrix, Davidson *et al.* (2013), prepared a fertilizer with controlled root targeted delivery system. The fertilizer maintained seed yield of wheat crops despite reductions of fertilizer use of up to 78%, with the possibility that this reduction could be increased to as much as 94% with further optimization.

Fu *et al.* (2016) prepared a methyl acrylic acid-modified bentonite (MAABT)/sodium polyacrylate (SPA) superabsorbent nanocomposite, in which the MAABT serves as a reinforcing agent for SPA, as well as a cross-linking joint to enhance the network of the nanocomposite. The interfacial compatibilization effect of the MAABT was understood by copolymerization of sodium acrylate and methyl acrylate groups which were chemically bonded on the surface of bentonite. With the fine dispersion of MAABT and strong interfacial interaction, the MAABT/SPA nanocomposite achieved a water absorbency that was as high as 1287 g/g under accurate controls. The thermal stability and water retention capacity of the nanocomposites were also improved with the incorporation of MAABT.

Chen *et al*. (2004) synthesized superabsorbent polymers (SAPs) by grafting copolymerization of acrylic acid and acrylamide onto starch by using γ-ray radiation technique and poly(ethylene glycol) (PEG) as a crosslinker. The samples were characterized by IR spectroscopy. The effect of various synthetic parameters such as irradiation dose, irradiation dose rate, monomer concentration, monomer/starch ratio, and PEG content were studied. The effects of different drying methods on water absorbency of the SAPs were also studied. The experimental results showed that the water absorbency of the SAPs depends largely on the specific conductance of water when the specific conductance is below500 µs/cm. The water retention of sand and soil was enhanced by using the SAPs. Effects of the SAPs on the germination of seeds and growth of young plants were investigated

Kiatkamjornwong *et al*. (2002) studied graft copolymerizations of acrylamide and/or acrylic acid onto cassava starch by a simultaneous irradiation technique using gamma-rays as the initiator with regard to various parameters of importance: the monomer-tocassava starch ratio, total dose (kGy), dose rate (kGy h-1), acrylamide-to-acrylic acid ratio, and the addition of nitric acid and maleic acid as the additives.

Loading of a superabsorbent composite (hydrogel) was done typically by two methods (Bajpai and Giri, 2002). In the first method, the compound to be loaded was added to the reaction mixture and polymerized *in situ* whereby the compound was entrapped within the gel matrix. In the second approach, the dry gel was allowed to swell in the compound solution and after the equilibrium swelling, the gel was dried and the material was obtained. There were some disadvantages to the first technique, for example the entrapped compound may influence the polymerization process and polymer network structure (Ward and Peppas, 2001); moreover, polymerization could have an adverse effect on the property of the entrapped compound. Urea, the one of the entrapped compound in the present study, might into change biuret under the effect of polymerization heat, which is harmful to crops.

2.2 Swelling mechanisms in hydrogel copolymer

Superabsorbent polymer composites (SPC) hydrogels relative to their own mass can absorbs and retain extraordinary large amounts of water or aqueous solution. These ultra high absorbing materials can imbibe deionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g). There are several mechanisms to the process of swelling, all of which contribute to the final swelling capacity.The polymer networkin (NCPC) is hydrophilic i.e. 'water loving' because it contains water loving carboxylic acid groups (-COOH). When water is added to NCPCs there is a polymer/solvent interaction; hydration and the formation of hydrogen bonds are two of these interactions.

Qin *et al.*, (2012) discussed the various factors affecting the swelling capacity of the superabsorbent nanocomposites. According to them, concentration of cross-linker, initiator, bentonite, and degree of neutralization of acrylic acid greatly affect the absorption of water by nanocomposites. They prepared superabsorbent nanocomposite using poly (acrylic acid-acrylic amide)/bentonite/urea and named as slow-release nitrogen fertilizer with water-absorbency (SRNFWA). First they observed the effect of the neutralization degree of acrylic acid, definedas the molar percentage of carboxyls in acrylic acid neutralized by NaOH aqueous solution. With increasing the neutralization degree gradually WA first increased and reached maximum (160 g g^{-1} in distilled water) at 70% neutralization degree and then decreased. They suggested that low degree of AA neutralization results in fast polymerization which gives oligomers. Because these oligomersare water soluble, they have low water absorbance capacity. However, higher degree of neutralization resulted in more carboxylate anions accumulation. These negative ions would set up an electrostatic repulsion among the network, which caused the expansion of the network and enhanced the WA.

Second factor they consider is initiator concentration, which determinesthe rate of polymerization, molecular weightof the polymer, and monomer conversion. By increasing the initiator concentration from 0.2 to 0.8 wt %, WA by SRNFWA increased. Because a very limited amount of free radicals was available at 0.2 to 0.8 wt % initiator concentration, so the polymerization rate was very slow depicting the low extensiveness and highWA of the system. However, further increase in initiator concentration (>0.8 wt %) increased the crosslinking density, which led to the decrease of the WA.

Third important parameter for WA is cross-linker concentration which controls the cross-linking density of the polymer network structure. Qin and co-workers (2012) found that with the increase of cross-linker concentration, the WA increased and became optimum at 0.04 wt % and above this optimal value, the WA decreased gradually till 0.1 wt %. The increase in cross-linker concentration up to the optimal value (0.04 wt %) could increase the cross-linking density and decrease the soluble part of the polymer, causing an increase in the WA. When the cross-linker content was higher than 0.04 wt %, the WA decreased. It could be explained on the basis of network water holding capacity as the concentration of cross-linker increases, the cross-linking intensity of the network increases reducing the space among the three-dimensional network for holding water and inhibits penetration of water molecules into the network. Hence, the WA of the SRNFWA exhibited a slow decrease with the increasing cross-linker content.

Fourth important factor is filler content in nanocomposite on the WA. The degree of swelling reached at maximum level when the concentration of Na-bentonite was 5.0 wt %. This may be due to that Na-bentonite particles serve as the cross-linking points chemically bonded with the monomers, which could improve the structure of network of the polymer composite. As Liang *et al.* (2007), reported the WA of poly (acrylic acid-co-acrylamide)/kaolin increase with the increase in kaolin content (0–10 wt %). Zhang *et al.* (2006) also verified the same results and believed that there might be some reaction between bentonite and polymer and analyzed it by IR spectra. Meanwhile, it is worthy to note that the addition of Na-bentonite could reduce the cost of the product. When the concentration of Na-bentonite was above 5.0 wt %, a large number of monomers were embedded by the Na-bentonite, which might alter the elastic response of the structure of polymeric network and could restrict the diffusion of small substances (such as H_2O, Na^+, etc.) into the polymer network and consequently reducing the WA.

Fernando *et al.*, (2013) studied swelling behaviour of starch Grafting acrylic acid on to starch leads to the formation of polymer chain which are covered with negative charges (COO^-) as shown in Figure 4 since negative charges will repel each other, the chain stretch out thereby providing spaces inside the polymer network which can absorb and retain a large volume of water or aqueous solution, e.g. body fluids or physiological salt.

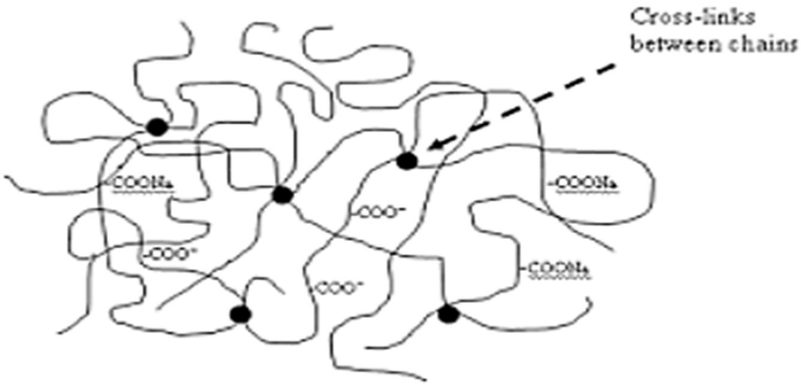

Fig. 4 Schematic of a cross-linked polymer network

Moreover, the hydroxyl groups from starch and the carboxyl groups from acrylic acid are hydrophilic and have a high affinity for water. Neutralization by adding sodium hydroxide replaces H^+ ions of carboxylic groups by Na^+. Upon contact with water these sodium ions are hydrated which reduce their attraction to the carboxylate ions. This allows the sodium ions to move more freely inside the network, which contributes to the osmotic driving force for the diffusion of the water in to the gel. Therefore, neutralization will increase the water absorption capacity.

Hua and Wang, (2009) found that the introduction of sodium humate into the sodium alginate-g-poly(acrylic acid) system could enhance the water absorbency and the superabsorbent containing 10 wt% sodium humate acquired the highest water absorbency (1380 g/g in distilled water and 83 g/g in 0.9 wt% NaCl solution).

2.3 Characterization of NCPCs

Numerous techniques for characterizing nanocomposites have been described in literature, including those based on microscopy (scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared (IR), and X-ray diffraction (XRD). A summary of experimental results obtained from many different papers is presented in Table 2.1.

2.3.1 X-ray Diffraction

Powder XRD pattern of clay and corresponding polymer/clay composites provide very important information regarding the basal spacing of clay and its corresponding polymer/clay composites. Sarkar *et al*, (2014) studied superabsorbent composite incorporated with 10 wt % clay of three types clay I (Kaolinite), clay II (Mica) and

Table 2.1 Summary of experimental results of XRD, FTIR, SEM and TEM obtained from many different papers

Study	System	XRD	FTIR	SEM/FESEM	TEM
Liu *et al*. (2013)	Chitin-based acrylate superabsorbents. (Chitin dissolved in 8 wt% NaOH/4 wt% urea aqueous solution by using a modified two times freezing–thawing cyclic (FTC) treatment)	**Chitin**: peaks at 9.53° 19.46°, 20.79°, 23.39° and 26.52° were observed in the 2θ range of 4–30°, indicated that raw chitin is α-chitin, **Treated chitin:** the peaks at 20.79°and 23.39° almost disappeared, due to distortion of crystal structure during the treatment **Grafted polymer:** for SAP diffraction pattern is highly similar to poly acrylic acid. The sharp crystalline reflections of chitin were concealed, and only observed a broad diffuse scattering peak, indicating that the grafting occurred.	**Chitin** absorption band at 3439 cm^{-1} in chitin was due to -OH stretching. **Treated chitin:** peaks at 3267 and 3107 cm^{-1} of N-H stretching vibration absorption were correspondingly weakened, **Grafted polymer:** bands at 3267 cm^{-1}, 3107 cm^{-1} were ascribed to N H stretching vibration, 1657 cm^{-1} to C=O stretching vibration of amide I and 1314 cm^{-1} to C-N stretching vibration and N-H in plane bending vibration, all disappeared. The absorption peaks at 1156 cm^{-1} and 1073 cm^{-1} showed the cancelation of the existence of the C-O- C bond. This information revealed that -OH, $-NH_2$, -NHCO and C-O-C of chitin took part in graft copolymerization reaction with AA.	**Chitin**: has an impacted multi-layered structure. **Treated chitin**: loose and undulant surface structure had been formed. It was convenient for the penetration of reagents into the chitin molecular chain **Grafted polymer:** surface became smooth, tight and porous, which was one of the reasons that the water absorption rate of SAP1 is not high. This change in surface morphology supported the occurrence of graft polymerization	

Wang and Wang,2010	sodium carboxymethyl cellulose (CMC)/ neutralized acrylic acid (NaA)/attapulgite (APT)	APT shows a strong reflection at 2θ = 8.41° with a basal spacing (d) of 1.051 nm. In nanocomposite reflection of APT still observed in the diffraction pattern of nanocomposite without obvious shift of peak position indicating that crystalline structure of APT was not destroyed during reaction, and the nano-scale APT fibril was retained and compounded with the CMC-g–PNaA matrix without intercalation.	Characteristic absorption bands of CMC at 1061, 1115 and 1159 cm^{-1} (stretching vibrations of C–OH) were obviously weakened after reaction. The new bands at 1716–1717 cm^{-1} (C = O stretching of –COOH) and 1576–1579 cm^{-1} (asymmetric stretching of –COO– groups) and at 1455 and 1410 cm^{-1} (symmetric stretching of –COO groups) appeared in the spectra of CMC-g–PNaA and CMC-g–PNaA/APT, revealed that NaA was grafted onto CMC backbone. The (Al)O–H stretching vibration at 3614 cm^{-1}, the (Si)O–H stretching vibration of APT at 3550 cm^{-1} and the –OH bending vibration at 1636 cm^{-1} disappeared in the spectrum of nanocomposite	APT exhibited a randomly oriented nano-scale fibril with the diameter of a single fibril less than 100 nm and the length of a single fibril is about several hundred of nanometers	The nano-scale APT fibril was also observed in the TEM image of the composite, which was almost embedded within the CMCg–PNaA matrix indicating that the APT nanofibril was uniformly dispersed in the nanocomposite without agglomeration and formed a homogeneous composition.

clay III (Smectite), observed that physical mixture of nanocomposite with clays showed no obvious differences in the position and intensities of the particular peaks for the corresponding clays but after the reaction i.e. after the formation of naonoclay polymer composites containing clays these peaks disappeared.

2.3.2 FTIR analysis

FTIR spectroscopy is a physical method for characterizing composite materials. It allows the identification of each component in the blend by the specific movement of each atom, which changes according to structure, composition and vibration mode of the sample (Jawhari *et al*., 1994; Evora *et al*., 2002).

Qin *et al.* (2012), found the peaks in Na-bentonite, urea, and poly (AA-co-AM)/Na-B/urea. The FTIR spectrum of the urea displayed the characteristic carbonyl peak at 1623 cm^{-1} (C=O), and two N─H absorbency bands at 3442 and 3348 cm^{-1}. The spectrum of the Na-bentonite mainly peaks characteristic at 1037 cm^{-1} correspond to the Si─O stretching, and at 915, 3624, and 3442 cm^{-1} correspond to the OH group. The three absorption peaks of OH group on Na-bentonite disappeared after the polymerization. However, the Si─O stretching still existed might be due to the grafted polymerization between –OH groups on bentonite and monomers occurred during the reaction course. Santiago *et al.* (2006) also reported the similar conclusion that hydroxyl groups on the surface of bentonite would react with the carboxyl group of poly (SA). So, Na bentonite particles could be acted as cross-link points developed some sort of bonding with the polymer.

Wu *et al.* (2003) reported that the characteristic absorption peak for –OH groups on kaolinite and starch, and $CONH_2$ group has changed after copolymerization reaction in starch-graft-acrylamide/kaoline composite which lead to the formation of network structure and water absorbing groups. By analyzing the infrared spectra, Lin *et al.* (2001) also showed that acrylic acid could graft onto mica and form the poly (acrylic acid)/mica superabsorbent composite.

The hydrogel composite was prepared by graft copolymerization of acrylic acid onto kappa carrageenan in the presence of a crosslinking agent and powdery bentonite by Hosseinzadeh *et al.* (2011). In the layer silicate structure of bentonite, the hydroxyl groups showed absorption bands at 3630 - 3680 cm^{-1}. The broad band at 3200 - 3400 cm^{-1} was due to stretching of –OH groups of the polysaccharide. The characteristic band at 1572 cm^{-1} was due to C=O asymmetric stretching in carboxylate anion that was reconfirmed by another peak at 1410 cm^{-1} which was related to the symmetric stretching mode of the carboxylate groups. The absorption band at 1722 cm^{-1} corresponded to the ester groups that were formed during the graft polymerization reaction. The carboxylate groups of the grafted poly (acrylic acid) could be reacted with the –OH groups on the bentonite surface results in the ester formation.

Kalaleh *et al.* (2013) analyzed the infrared spectra of bentonite powder and poly(acrylate-co-acrylamide)/bentonite composite.In the spectrum of the bentonite, they reported that the peaks observed were at 3614 cm^{-1} and 3547 cm^{-1} for the OH groups stretching in Al-OH and Fe^{3+}-OH respectively, and at 1029 cm^{-1} corresponding to Si-O stretching. The peaks at 1655 cm^{-1} and at 3414 cm^{-1} were assigned to OH deformation and OH stretching in H-O-H respectively. In the spectrum of the copolymer hydrogel, the peaks observed at 3443 cm^{-1} and at 3184 cm^{-1} correspond to O-H and N-H stretching respectively. The absorbance at 2925 cm^{-1} was assigned to –C-H stretching of the acrylate group. The peak at 1676 $cm^{-1}$and at 1726 cm^{-1} were assigned to C=O stretching of the acrylamid groups and acrylate groups, respectively. The peak at 1168 cm^{-1} was attributed to –COO stretching of the acrylate group and the peak at 1559 cm^{-1} was assigned to –COONa group.

2.3.3 Scanning electron microscopic technique (SEM)

SEM is a technique that allows the shape and surface feature of clay and composites to be viewed in three dimensions. When a scanning electron microscope is used, the sample is coated with a thin layer of a reflective metal and then irradiated with a beam of electrons. The electrons are reflected back to a sensor, allowing surface feature of composite to be seen in great detail (Thomas and Atwell, 1999). This technique has a resolution power at least 10 times greater than that of light microscopy (Simao and Cordenunsi, 2010).

Sirousazar *et al.* (2012) presented excellent SEM images obtained from the fractured surface of pure polyvinyl alcohol (PVA) hydrogel and nanocomposite hydrogels containing 5 and 15 wt % of kaolinite. They observed a filamentous morphology with more packed structure in the fracture sections of nanocomposite hydrogels compared to the pure PVA hydrogel which could be attributed to the increase in the crystallinity of PVA chains in presence of kaolinite silicate layers.

Gao *et al*. (2009) studied the degradation behavior of hydrogel based on oxidised sodium alginate (OSA) crosslinked with Ca^{2+} n phosphate buffer solution (pH = 7.4) and Tris-(hydroxymethyl) aminomethane–HCl (pH = 7.4) at 37 ^{o}C. In the study, SEM images of sodium alginate and OSA hydrogels were obtained. The SEM images showed that sodium alginate, 10 % OSA and 30 % OSA hydrogels demonstrated laminated structures while 50 % OSA hydrogel showed a different structure from sodium alginate, 10 % OSA and 30 % OSA hydrogels.

In 2010, Isiklan and colleagues reported on the preparation of graft copolymers of NaAlg with IA in aqueous solution using benzoyl peroxide (BPO) as the initiator under nitrogen gas atmosphere. SEM picture exhibited that the surface of the NaAlg-*g*-PIA copolymer was a more spongy structure than that of NaAlg. The results obtained also showed that by varying the reaction conditions such as reaction time, temperature, concentration of monomer and initiator, control of the grafting parameters was possible.

2.3.4 Transmission electron microscopic observations (TEM)

TEM is characterized by a resolving power 1000 times greater than that of light microscopy (Simao and Cordenunsi, 2010). It is commonly used together with XRD to determine if an intercalated or exfoliated nanocomposite was formed or if the nanofiller and polymeric matrix were miscible (Kumar *et al.*, 2010).

The microstructure of nanocomposite hydrogel containing 5 wt % kaolinite was also observed using transmission electron microscopy (TEM). The image obtained was clearly in accordance with the XRD results and proved the intercalated morphology for PVA/kaolinite nanocomposite hydrogels (Sirousazar *et al.*, 2012).

2.3.5 SEM-EDX measurements

The morphology and relative elemental concentration of the samples were analyzed by means of scanning electron microscopy (SEM) equipped with an energy dispersive analysis system of X-ray spectrometer-EDX. The sample was dispersed over a carbon tape pasted on the surface of a metallic disk. Then, the disk was coated with gold in an ionization chamber and analyzed.A novel poly(acrylic acid-co-acrylamide) $AlZnFe_2O_4$/potassium humate superabsorbent hydrogel nanocomposite (PHNC) was synthesized. The chemical composition of the nanoparticles was determined by Energy Dispersive X-ray analysis (EDX), which showed that nanoparticles contain only Fe, Zn, Al and O with no traces of by-products (Shahid *et al.* 2012).

2.4 Evaluation of nanocomposites for controlled release of N in water and soil

Nitrogen is the most vital nutrient for crops. Among the nitrogen fertilizers, the most widely used one is urea because of its high nitrogen content and comparatively low cost of production. However, due to surface runoff, leaching, and vaporization, the utilization efficiency or plant uptake of urea is generally below 50% (Abraham *et al.*, 1996). One of the best mechanisms to overcome these shortcomings is use of slow release fertilizers. Rashidzadeh and Olad, (2014) investigated the release pattern of fertilizers (NPK) from the encapsulated fertilizer made with sodium alginate, acrylic acid, acrylamide, montmorillonite by conductivity measurements, reflecting the total concentration of fertilizers as a function of time in water. They found complete release of fertilizers in NPK fertilizer was released within 4 h. The release of fertilizer from Hyd/NPK was 29.53%, 39.23% and 68.34% in the first day, one week and one month, respectively. In contrast, in the caseof Hyd/MMT/NPK release of fertilizer was 14.66% on the first day,28.54% on one week, and 57.66% on one month.The fertilizer release behaviors of Hyd/NPK and Hyd/MMT/NPK in soil was 38.23%, 58.01%, 73.1% and 13.7%, 39.42%, 60.69% within 1, 7, and 30 days, respectively.

Wu *et al.*, (2008) studied the slow release behavior from the double-coated slow-release NPK with superabsorbent and water-retention (DSFSW) fertilizer, made by poly(acrylic acid)/diatomite -containing urea (the outer coating), chitosan (the inner coating), and water-soluble granular fertilizer NPK (thecore). The N in DSFSW released 11.9%, 17.8%, and 73.2% by the 3rd, 5th, and 30th days.The P in DSFSW released 3.9%, 8.2%, and 64% by the 3rd, 5th, and 30th days. The K in DSFSW released 2.3%, 6.4%, and 68% by the 3rd, 5th, and 30th days. These results indicated that the slow-release properties of DSFSW conformed to the standard of slow-release fertilizers of the Committee of European Normalization (CEN) (Trenkel, 1997).

2.5 Degradation study

Biodegradable polymers are a type of macromolecules which are able to breakdown into smaller compounds or completely degraded in biologically active environments (Baker *et al.*, 2009). The breakdown process is normally caused by microorganisms

(Cosgrove *et al.*, 2007), however biodegradation can also occur through hydrolysis and oxidation processes in biological environment.

Microorganisms of the soil are the main parties which contribute to majority of polymer degradation (Cosgrove *et al*., 2007). Hence, biodegradability of a polymer depends on the types of biological enzymes and microorganisms present in the soil. Nevertheless, the specific populations desirable for a particular degradation are dependent upon numerous environmental factors in the soil, such as soil moisture content, pH, soil organic matter, and etc. (Tangjang *et al*., 2009). Biodegradable polymers are a type of macromolecules which are able to breakdown into smaller compounds or completely degraded in biologically active environments (Baker *et al*., 2009). The breakdown process is normally caused by microorganisms (Cosgrove *et al.*, 2007), however biodegradation can also occur through hydrolysis and oxidation processes in biological environment.

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There is a worldwide research effort to develop biodegradable polymers for agricultural applications or as a waste management option for polymers in the environment. Until the end of the 20th century, most of the efforts were synthesis oriented, and not much attention was paid to the identification of environmental requirements for, and testing of, biodegradable polymers. Consequently, many unsubstantiated claims to biodegradability were made, and this has damaged the general acceptance.

ASTM standard D-548894d defines the term “biodegradation” for the materials “capable of undergoing decomposition into carbondioxide, methane, water, inorganic compounds or microbial biomass in which the predominant mechanism is the enzymatic action of microorganisms, which can be measured by standard tests, in a specified period of time, reflecting available disposal conditions”.

The chemistry of the key degradation process of polymeric materials is represented by Eq. (11.1) and (11.2), where $C_{polymer}$ represents either a polymer or a fragment from any of the degradation processes

Aerobic biodegrada0tion:

$$C_{polymer} + O_2 \rightarrow CO_2 + H_2O + C_{residue} + C_{biomass}$$

Anaerobic biodegradation:

$$C_{polymer} \rightarrow CO_2 + CH_4 + H_2O + C_{residue} + C_{biomass}$$

Lanthong *et al*, (2006) prepared starch-based superabsorbent polymersby grafting of poly (acrylamide-co-(itaconicacid)) onto starch, where the starch andpoly (acrylamide-co-(itaconic acid)) ratio is in the range of 1:4–2:1. Their absorption capacity differed from the amount of itaconic acid and starch content. The biodegradation of graft copolymer was investigated by enzymatic method using a-amylase. After hydrolysis by enzyme, the amount of reducing sugar was determined by DNS method

Lee and co-workers (2005) prepared biodegradable SAPs, hydrolysed AN-grafted-NaAlg copolymers by graft copolymerisation of AN on NaAlg, followed by subsequent hydrolysis of the resulting grafted copolymer. The authors concluded that the variables which affected the swelling capacity of the SAPs produced were the percentage add-on, graft copolymerisation conditions and hydrolysis conditions. Furthermore, compared with commercial SAPs, good biodegradability was shown by the SAPs during enzymatic hydrolysis tests.

2.6 Effect of slow release superabsorbent fertilizers on growth and yield of crops

Effectiveness of superabsorbent polymers (SAP) in agriculture to improve soil moisture retention capacity and improving plant growth has been assessed in several investigations (Anupama *et al.*, 2007; Singh *et al.*, 2011). Islam *et al.* (2011) studied the effectiveness of SAP under three irrigation levels (adequate, moderate and deficit) using SAP at 30 kg ha^{-1}. They observed that after eight weeks of sowing, plant height and leaf area increased significantly by 41.6 and 79.6% under deficit irrigation for SAP treatment. The SAP had little effect on shoot dry mass under adequate and moderate irrigation but increased it significantly by 133.5% under deficit irrigation. Similarly, the efficiency of water use also increased by 97.1%. The superior growth and water use efficiency of corn treated with SAP under deficit irrigation was ascribed to maintenance of higher relative water contents in leaves as well as intercellular carbon dioxide concentration, net photosynthesis and transpiration rate.

In practice, however, SAP always increases farmers' financial burden, but does not significantly bring an augment of the crops yield if it is utilized without supply of fertilizers. Recently, research efforts focused on incorporating fertilizers in to superabsorbent polymeric networks to supply water and nutrients simultaneously through a single formulation (Liang *et al*., 2007; Zhong *et al*., 2013). A slow-release fertilizer was prepared by covalently immobilizing urea on a biodegradable polymer matrix consisting of acrylamide (AAm) and maleic acid (MA) by Rahman *et al*. (2008) and the growth and yield from green chilli *Capsicum annuum* plants in presence the prepared slow release N-fertilizer was investigated. Results showed that P (AAm-MA) U contained 32.85% N and the solvency in aqueous media reduced by 297 times as compared to urea. P (AAm-MA) U showed improved yield in terms of average plant size over the cultivation period. The N release behaviour in soil during cropping and plant uptake of N suggested that P(AAm-MA)U can be used as slow-release N-fertilizer.

Sarkar *et al*. (2014) studied the P and N releasing behaviour from fertilizer loaded nanoclay superabsorbent polymer composite (NCPC) and to test its effectiveness as a carrier of slow release fertilizer using pearl millet (*Pennisetum glaucum*) as test crop grown under Inceptisols. Results revealed that addition of high dose of fertilizer NCPC-H resulted in 18% additional biomass yield and 17% and 11% additional P and N uptake by pearl millet over conventional fertilizer (CF-H), respectively. Similarly, at low dose of fertilizer (LDF), biomass yield, P and N uptake increased to 26, 23 and 16%, respectively, under NCPC (NCPC-L) treated soils than that in CF (CF-L) treated soil.

Xu *et al.* (2013) studied the yield, and N use efficiency of wheat after applying biodegradable polymer (poly (γ-glutamic acid)) coated nitrogen fertilizer. Results revealed a statistically significant increase in winter wheat, number of tillers, seed number per spike, and yield. The highest grain yield of 7435.69 ± 55.91 kg ha^{-1} was obtained after γ-PGA application in the field experiment, which was 7.17% higher than the urea control.

2.7 Effect of slow release superabsorbent fertilizer on nutrient availability in soil and uptake in plants

Sarkar & Dutta (2014) studied the effect of fertilizer loaded nanoclay superabsorbent polymer composite (NCPC) on dynamicsof P and N availability and their uptake by pearl millet. Three types of NCPCs (I, II and III) synthesized from Kaolinite, Illite and Smectite dominated nanoclays, respectively were loaded separately with di-ammonium phosphate (DAP) and urea solution and applied in the crop at high (NCPC-H, CF-H) and low (NCPC-L, CF-L) rate. Release of P and total mineral N from NCPCs loaded with DAP and urea, respectively, were compared with corresponding conventional fertilizer (CF). P availability (Olsen-P and 0.01M $CaCl_2$-P) under NCPC treated soil was higher than its corresponding CF treatment for at least up to 40DAS. Availability of P under NCPC-L treatment remained at par with P availability under CF-H treatment at critical crop growth stages (20 to 40 DAS). The total mineral N concentration in the soil of the NCPC-H treatment was lower than that in the CF-H treatment for the early sampling period (10 DAS). After that time the NCPC-H treatment tended to maintain a higher concentration of total mineral N in the soil, although the differences were not always statistically significant. Similarly, at early stage (10 DAS) treatment CF-L maintained significantly higher concentration of total mineral N than NCPC-L treatment, thereafter the trend reversed although the differences were not always statistically significant. Addition of NCPC-H resulted in 18% additional biomass yield and 17% and 11% additional P and N uptakeby pearl millet over CF-H, respectively. Similarly, at LDF, biomass yield, P and N uptake increased to 26, 23 and 16%, respectively, under NCPC (NCPC-L) treated soils than that in CF (CF-L) treated soil. Significant build-up in different non labile pools of inorganic P fractions (Al-P, Fe-P, occluded-P, Ca-P) was recorded on addition of CF as compared to NCPC application, irrespective of fertilizer doses.

2.8 Effect of slow release superabsorbent fertilizers on NUEs in crops

The estimation of nitrogen use efficiency (NUE) in crop plants is crucially needed to assess the fate of applied nitrogen and their role in improving maximum economic yield through efficient absorbed or utilization by the plant. Cereals require N-fertilizers to produce maximum yields and high protein content (Ortiz – Monasterio *et al.*, 1997; Barraclough *et al.*, 2010). However, NUE in cereals is generally poor, where it is estimated 30-40% of the total of N-fertilizers applied is actually harvested in the grain. The reminder of the applied N is lost to the soil, where often-excessive application can affect natural ecosystems through N pollution. Loss of N also contributes to significant direct economic losses to the grower particularly when N fertilizer costs are high (Raun and Johanson 1999; Glass *et al*., 2003; Gruber and Gilloway 2008). It has been estimated that an increase in NUE by one percent is worth as much as USD $234 million (Magen and Nosov 2008). Therefore, initiatives to improve NUE will be important in order to minimize both N-fertilizer losses and the direct production costs of the crop. On the basis of field experiments, (Cassman *et al*., 2002) reported N recovery in wheat varied from as low as 18 percent under unfavourable weather to 49 percent under favourable weather conditions. One of the main causes of low NUE in actual N management practices is the limited synchrony between N soil availability and crop demand (Raun and Johnson 1999; Cassmann *et al*., 2002; Fageria and Baligar 2005). Consequently, many different agronomic avenues are pursued to improve NUE in cereal crops. Use of slow release N fertilizers application to a reasonable rate, therefore, is considered essential to reduce environmental costs, without sacrificing grain yield.

Xu *et al.* (2013) studied the yield, and N use efficiency of wheat after applying biodegradable polymer (poly (γ-glutamic acid)) coated nitrogen fertilizer. They found that the N recovery efficiency increased by 11.81%–14.00% and 11.30%–11.38% after the application of γ-PGA in pot and field experiments, respectively.

2.9 Soil organic carbon and nitrogen

Soil organic matter has long been considered the key quality factor of soil. It is a source and a sink of plant nutrients in the soil, and is important in maintaining soil tilth, improving aeration and infiltration of water, promoting water retention, reduction erosion, and controlling the efficacy and fate of applied pesticides (Gregorich *et al*., 1993). Soil organic matter plays a key role in soil biological and chemical processes, and changes in soil organic matter strongly influence soil N turnover because of the importance of available C for microbial immobilization (Bird *et al*., 2002). Soils with higher organic matter contents may immobilize more N and reduce N loss to the environment. Otherwise, the depletion of available C will cause more rapid N turnover and losses (Compton and Boone, 2002). In addition, changes in N availability can also alter soil C turnover (Neff *et al*., 2002). There is no doubt that higher crop production in response to mineral N fertilizer application results in greater root exudates and more crop residues, thereby enhancing SOC sequestration in agricultural soils (Christopher and Lal, 2007).

In addition increasing N fertilizer application can stabilize organic matter (Swanston *et al*., 2004) and retard the mineralization of older soil organic matter (Hagedorn *et al*., 2003). N fertilization plays a positive role in enhancing the SOC (Swanston *et al*., 2004), (Malhi *et al*., 2003; Blair *et al*., 2006; Jagadamma *et al*., 2007; Lemke *et al*., 2010). However, the addition of N fertilizer has also been reported to have a negative or no effect on SOC accumulation (Mack *et al*., 2004; Dolan *et al*., 2006; Fonte *et al*., 2009; Liu and Greaver, 2010; Lu *et al*., 2011). Changes in the decomposability of fresh plant litter and soil organic matter fractions, the stability of soil aggregates, and/or shifts in the microbial community can beused to explain the decreases in SOC attributed to N fertilizer addition (Mack *et al*., 2004), (Fonte *et al*., 2009). Therefore, achieving a better understanding of the interaction between N fertilizer and SOC in agricultural soils is essential for maximizing SOC storage and minimizing potential N losses.

2.10 Soil microbial biomass

Soil organic matter, though usually comprising less than 5% of a soil’s weight, is one of the most important components of a field ecosystem. It serves as soil conditioner, nutrient source, substrate for microbial activity, preserver of the environment and major determinant for sustaining agricultural productivity (Schnitzer, 1991). Changes in SOC may be difficult to monitor in the short term because of (1) low magnitude of change, (2) high background carbon levels and (3) high natural variability of soils. The living and the most active part of SOC i.e., microbialbiomass carbon (MBC), rather than total amounts of SOC, therefore, has been suggestedas a useful and more sensitive measure of a change in SOC status (Powlson *et al*., 1987; Friedel *et al*., 1996). With a comparatively rapid rate of turnover of 1–2 years, it is possible to detect changes in microbial fraction long before they are detectable in the total organic matter (Jenkinson and Ladd, 1981). The MBC normally comprises 1–3% of the total SOC. However, this percentage, the ‘microbial quotient’, has been reported to change in a consistent way and to provide a useful lindicator of the soil processes (Anderson and Domsch, 1989).

Banerjee *et al*. (2006) conducted a field experiment to study the soil organic carbon (SOC) and soil microbial biomass carbon (MBC) dynamics in the rice-wheat systems. Use of organic amendments and puddling of soil before rice transplanting increased SOC and MBC contents. Microbial biomass carbon showed a seasonal pattern. It was low initially, reached its peak during the flowering stages in both rice and wheat and declined thereafter. Microbial biomass carbon was linearly related to SOC in both rice and wheat indicating that SOC could be used as a proxy for MBC.

Xu *et al*. (2013) studied the soil microenvironment of wheat after applying biodegradable polymer (poly (γ-glutamic acid)) coated nitrogen fertilizer. Results revealed a statistically significant increase insoil microbial biomass N (SMBN) after γ-PGA application to 3.70–7.91 mg kg^{-1} and increased by 17.35%–37.08% at the tillering stage, and then further increased to 9.65–13.85 mg kg^{-1} and increased by 49.03%–70.38% compared with control urea treatment at the jointing stage.

Rakshit & co-workers (2015) investigate the effect of recommended 100% nitrogen, phosphorus and potassium (NPK) to super-optimal doses (200% NPK) of mineral fertilizers on microbial biomass and organic carbonat various phenological stages of wheat growth. Excessive mineral fertilizer did not affect the soil organic carbon (SOC), but SOC was found to be higher at anthesis stage (16.67% and 12.32% higher over maturity and Crown Root Initiation (CRI) stage, respectively). Microbial biomass carbon (MBC) was found to be higher (252.06 µg g^{-1} dry soil) at anthesis stage of wheat growth, which declined to 213.28 µg g^{-1} dry soil at maturity. Super-optimal application of fertilizers led to significant increase in microbial biomass nitrogen (MBN) at anthesis (+17.7%) and maturity stage (+15.55%) over the 100% recommended dose of fertilizer.

2.11 Enzyme activity in soil

Among the many biological properties that have potential as sensitive indicators of soil quality and fertility, enzyme activities often provide a unique integrative biological assessment of soil function, especially those that catalyze a wide range of soil biological processes, such as dehydrogenase, urease and phosphatase (Nannipieri *et al*. 2002). Soil enzymes play key biochemical functions in the overall process of the transformation of organic matter and soil nutrient cycling in the soil system (Burns, 1978). The agricultural significance of soil enzymes has been progressively expanded since the first report on soil enzymes was written about a century ago (Shi, 2011). Soil enzymes, which were once used as descriptive parameters, are now appreciated for their multiple functions in microbial activities, soil processes and ecosystem responses to management and global environmental change (Finzi *et al.*, 2006).

Enzymes play an important role in the cycling of nutrient in nature and because their activity is sensitive to agricultural practices they can be used as an index of soil microbial activity and fertility (Benitez *et al.*, 2000). Earlier, the emphasis had been placed on the conventional physical and chemical properties as indicators of soil fertility rate, but often these properties responded slowly to management practices and were found to be not sensitive enough to detect changes in soil properties that are caused by agricultural management practices, especially in the short-term (Mijangos *et al.*, 2006). Therefore, there is a need to find suitable tools that reflect the influence of management practices in order to observe possible changes (Piotrowska *et al.*, 2012). Biological indicators, such as soil microbiological biomass and enzymatic activity, seem to be better indicators since they respond much more quickly to both natural and anthropogenic factors in comparison with other variables (Garcia *et al.*, 2000). Thus, they may be useful as early indicators of biological changes in soil (Bandick and Dick, 1999, Masciandaro *et al.*, 2004). Soil enzyme activities are strongly affected by the agricultural management practices and have been used as indicators of irrigation (Zhang and Wang 2006), the application of inorganic fertilizers and organic amendments (e.g., Sinsabaugh *et al.*, 2005; Benitez *et al.*, 2004; Iyyemperumal and Shi 2008; Guo 2011), different management and farming systems (e.g., Dodor and Tabatabai, 2003; Klose *et al.*, 1999; Gajda and Martyniuk, 2005) and soil tillage (e.g., Acosta-Martínez and Tabatabai 2001; Ulrich *et al.*, 2010). Enzymatic activity was found to be the most strongly influenced soil property under intensive agricultural practices as compared with other biochemical parameters (Saviozzi *et al.*, 2001).

Among the different farming practices, the management of mineral fertilizers and organic amendments could have a major impact on soil fertility, thus influencing the quantity and quality of organic residues and nutrient inputs that enter the soil and the rate at which the residues and organic matter are decomposed (Gerzabek *et al.*, 2006). The influence of inorganic fertilization on the soil enzyme activity depends on the dose of the fertilizer and the time of its application, the soil type, climatic conditions and the enzyme itself (Gianfreda and Bollag, 1996). Studies on the effect of inorganic N fertilization on enzyme activities have led to contradictory results (Gianfreda and Ruggiero, 2006). Some previous studies have shown that N fertilization can accelerate the activity of some C, N and P cycling enzymes, like cellulases (Sinsabaugh *et al.*, 2005), urease (Saiya-Cork *et al.*, 2002) and phosphatases (Guo *et al.*, 2011 ; Saiya-Cork *et al.*, 2002) or decrease the activity of urease (Burket and Dick 1998), cellulases (Sinsabaugh *et al.*, 2005), peroxidase (DeForest *et al.*, 2004), proteases (Giacometti *et al.*, 2013), while some other enzymes are not affected with increasing N fertilizer application (Klose *et al.*, 1999 ; Klose and Tabatabai 2000). More often, however, enzyme activities increased when organic and inorganic N fertilizers were added together (Eivazi *et al.*, 2003). Mineral N can directly affect the microbial production of soil enzymes but the effect varies with the type of soil and the enzyme as well as with the kind of enzymatic reaction (Iyyemperumal and Shi 2008), which is possibly due to changes in the composition of the soil microbial community and, therefore, the enzyme production (Burns 1978; Iyyemperumal and Shi 2008). On the other hand, N fertilization, especially in mineral forms, may have an indirect effect on the activities of soil enzymes via changes in soil properties, such as soil reaction (Gianfreda and Ruggiero 2006).

Soil enzyme activity can be affected by the presence and nature of plant cover (Gianfreda and Bollag 1996). Although most of the soil enzyme activities originate from microorganisms, plant roots are an important source of extracellular enzymes in soil. Juma and Tabatabai (Juma and Tabatabai 1988) showed that sterile corn and soybean roots contain acid phosphatase, but not alkaline phosphatase activity. Although there was no clear relationship between arylsulfatase activity and root distance; enzyme activity tended to be higher close to the root surface (distance 0.25 mm) as compared with the distance of 0.75 mm in all of the crop species (*Barssicanapus, Sinapus album, Triticumaestivum, Loliumperenne*) (Knauff *et al.*, 2003). Plants actively respond to an insufficient S supply by producing and excreting sulfatases, which may help them to exploit the organic soil S, compounds (Knauff *et al.*, 2003). The arylsulfatase activity that is found in the root protein extracts cannot originate from soil bacteria, since the seeds and seedlings had no contact with the soil. This could be explained by the fact that higher plants possess their own arylsulfatases that are inducible under an S deficiency or that seed-borne bacteria that colonize the intercellular sites within the root such as endophytes are responsible for the enzyme activity (Knauff *et al*., 2003).

Plant roots stimulate enzyme activity by creating advantageous conditions for microbial activity (Castellano and Dick 1991). Highest higher enzymatic activity in the plant rhizosphere than in bulk soils was found in many researches, which may be explained by the development of a large population of soil microorganisms in the vicinity of roots that metabolize amino acids, sugars, organic acids and other compounds that are exuded by roots (Knauff *et al.*, 2003; Tarafdar and Chhonkar 1978). Leguminous plants have the potential for biological N fixation and this could stimulate the activity of the enzymes that are involved in the N cycle (urease and protease-BBA) (Roldán *et al.*, 2003). In crop systems that involve both leguminous and nonleguminous plants, the leguminous rhizosphere showed a higher activity of acid, neutral and alkaline phosphatase as compared with the non-leguminous plant rhizosphere (Tarafdar and Chhonkar 1978).

The highest catalase activity was recorded in soil under wheat, soybean and winter legume crops, while the lowest activities were found in soil bearing corn and cotton and during the winter fallow period in the rotation system at the Agronomy farm of the Alabama Agricultural Experimental Station (USA) (Rodríguez-Kábana and Truelove 1982). The highest activity of arylsulfatase among different crop species was with Cruciferae due to their high S demand (Knauff *et al.*, 2003). Soil that was under permanent grassland had 1.5 times higher dehydrogenase activity and almost a two times higher acid phosphatase activity than no-till and conventionally tilled soils (Carpenter-Boggs *et al.*, 2003). Higher arylsulfatase activity was noted in soils from a permanent pasture and an alfalfa field than from cultivated wheat fields (Germida *et al*., 1992). Both longterm leguminous cover cropping and the direct incorporation of green manure increase the soil protease activity due to the enhancement of soil organic matter and the stimulation of soil microbial activity (Dinesh *et al*., 2004).

2.11.1 Dehydogrnase activity (DHA)

Soil dehydrogenases are the major representatives of the oxidoreductase enzymes class. Lenhard (Lenhard, 1956) was first to introduce the concept of determining the metabolic activity of soil microorganisms by measuring the activity of dehydrogenases because of its simplicity as compared to other quantitative methods.

The activity of the DHA reflects the total range of the oxidative activity of soil microorganisms and may be considered a good indicator of the oxidative metabolism in soils, and thus, of microbiological activity (Gu *et al.*, 2009). Dehydrogenases oxidize soil organic matter by transferring protons and electrons from organic substrates to inorganic acceptors (Kumar *et al.*, 2009). Many specific dehydrogenases transfer hydrogen on either the nicotinamide adenine dinucleotide or the nicotinamide adenine dinucleotide phosphate. Throughout mentioned co-enzymes hydrogen atoms are involved in the reductive processes of biosynthesis. These processes are part of the respiration pathways of soil microorganisms and are closely related to the type of soil and air-water conditions (Wolińska and Stępniewka 202).

Kanchikerimath and Singh (2001) found that optimum and balanced application of inorganic fertilizers and organic amendments led to significant increase in dehydrogenase activity. In the most heavily fertilized treatment (150% NPK), a large and highly significant reduction in dehydrogenase activity was observed. This suggests that dehydrogenase was highly sensitive to the inhibitory effects associated with large fertilizer additions.

Patra *et al.* (2006) reported that the mean dehydrogenase activity in rice soil at 10 days after top dressing (i.e. 40 days after transplanting) varied from 50.4 mg in control to 103.2 mg TPF $kg^{-1}24\ h^{-1}$ in urea treated soil significantly lower values of dehydrogenase activity were measured in soils where encapsulated calcium carbide (ECC) was applied. Similarly, in wheat the dehydrogenase activity was as much as 78 mg TPF $kg^{-1}24\ h^{-1}$ in urea treated soil and ECC application caused a significant suppression (to 67–68 mg TPF $kg^{-1}24\ h^{-1}$) in the dehydrogenase activity. They suggested that slow release of acetylene (C_2H_2) from ECC reduced ammonia mono-oxygenase with reducing population of ammonium oxidizing bacteria, having potential to retard the enzyme activities in favor of C and N conservations in a semi-arid agro-ecosystem.

Islam and Borthakur (2016) investigated the influence of different growth stages of rice on soil microbial biomass and enzyme activities like dehydrogenase. They found the progressive decrease in the dehydrogenase activity from 90 DAT to 150 DAT (flowering to late maturity stage of the rice). The higher dehydrogenase activity at 90 DAT was likely due to high C input in the soil in the form of root mass that enhanced microbial activity. The relation between dehydrogenase activity and C inputs has been well established (Maurya *et al.* 2011).

Hernandez *et al*., (2015) evaluated the impact of the e addition of large amounts of an organic amendment on the recovery of the physical, chemical and, particularly, the microbiological properties of a marginal semiarid degraded soil and on increasing the soil organic C pool. Compost addition increased b-glucosidase and phosphatase activity, activating the dynamics of the cycles of C and P and the mineralization processes associated with these cycles. These results, together with the increases detected in the amended soils in the basal respiration rate, ATP and dehydrogenase activity, indicate a positive effect of the amendments on the activity of the microbial populations (Ros *et al*., 2003; Celis *et al*., 2009). Furthermore, this effect was greater at the higher application rate. Such substrates stimulate enzyme synthesis and improve the microbiological quality of the soil. In addition, the improvement of the physical conditions of the soil resulting from the addition of compost produces aeration and humid conditions in the soil, creating a more favorable environment for microbial growth and activity.

2.11.2 Urease activity

The Urease (UR) enzyme is responsible for the hydrolysis of urea fertilizer into NH_3 and CO2 with the concomitant rise in soil pH and N loss to the atmosphere through NH_3 volatilization (Fazekašová 2012). Urease can be produced by bacteria, yeasts, fungi and algae, as well as plants (Follmer 2008). Urease may be synthesized constitutively in some organisms, but most often urease expression is under N regulation (Mobley *et al*., 1995). The enzyme synthesis is inhibited when cells grow in the presence of a preferred N source such as NH_4^+ (Geisseler *et al*., 2010). In contrast, urease production is activated in the presence of urea or alternative N sources (Mobley *et al*., 1995). Due to its role in the regulation of N supply to plants after urea fertilization, soil urease activity has received a great deal of attention since it was first reported (Rotini 1935). Urease has been widely used to evaluate changes in soil fertility since its activity increases with organic fertilization and decreases with soil tillage (Saviozzi *et al*., 2001).

Sharma *et al*., (2015) conducted a field experiments for two years to investigate the effect of tillage, irrigation regimes, and integrated nutrient management practices on the soil enzymatic and microbial activities. The soil glucosidase (67.35%) and urease (106.75%) increased under conservation tillage compared with conventional tillage; largest increase was observed when a combination of 50% farm yard manure + 25% biofertilizer + 25% green manure (GM) was used in place of recommended dose of nitrogen (RDN) or when 25% RDN was replaced with biofertilizer or GM as nutrients in combination with conservation tillage and optimum water supply (three-irrigations) with a few exceptions. The present study has suggested that resource management practices significantly improved soil enzymatic and microbial activities under conservation tillage and optimal water supply which reduce the dependence on chemical fertilizers and make rice cultivation sustainable.

2.11.3 Phosphatase activity

Phosphatases are a group of enzymes that are of great agronomic value because they catalyze the hydrolysis of organic phosphorus compounds and transform them into an inorganic form of P, which is then assimilated by plants and microorganisms (Amador *et al*., 1997). Agricultural soils contain phosphatases in varying amount depending on the microbial count, the amount of organic materials, mineral and organic fertilizers, tillage and other agricultural practices (Banerjee *et al*., 2012). The relationship between the available P content and phosphatase activity in soil is complex. A positive, negative or no relationship can be observed between these properties. Generally, a significant and positive relationship between phosphatase activity and P availability (Gianfreda and Bollag, 1996; Šarapatka 2003) is obtained in soils that are not fertilized and/or those that have small amounts of nutrients in which a P deficiency occurs. An inverse relationship between these two parameters is usually observed in soils that are fertilized with P and/or those with a sufficient content of available P. There are studies that show that phosphatase activity is inversely proportional to the plant available P content (Amador *et al*., 1997; Šarapatka 2003; Sinsabaugh *et al*., 1993), which confirms the thesis that the production and activity of soil phosphatases is connected with the demand of microorganisms and plants for P. Phosphatases are typical adaptive enzymes and their activity increases when the plant available P content decreases (Nannipieri 1994). Kinetics studies indicate that orthophosphate ions, which are the product of the reaction that is conducted by the phosphatases, are competitive inhibitors of their activity in soil (Juma and Tabatabai 1978). When no relationship is seen, P may not limit the study system and some other factors may influence the enzyme production and activity (Olander and Vitousek 2000).

Gaind and Nain (2011)accounted soil quality parameters and wheat (*Triticum aestivum* HD-2285) yield by *insitu* incorporation of paddy straw, inoculated with two cellulolytic and one lignolytic fungi. The paddy straw amended with $N_{60}P_{60}$ resulted in dehydrogenase, alkaline phosphatase, cellulase, cellobiase and urease activity, statistically at par with $N_{120}P_{60}$ fertilized or fungal inoculated paddy straw treatments. The $N_{60}P_{60}$ treatment also showed highest soil microbial biomass. Higher wheat yield in this treatment, compared to recommended dose of chemical fertilizers made the use of natural resources a profitable option.

2.12 N_2O emission from crop fields

The Indo-Gangetic Plain (IGP) of South Asia is home to nearly one billion people. In IndianI GP, Rice (*Oryza sativa* L.)–Wheat (*Triticum aestivum* L.) (RW) is the dominant cropping system, occupying about 10.3 million ha and accounts for 23% and 40% of India’s rice and wheat area, respectively (Gathala*et al.* 2013). Rice is grown during the summer season (June to October) and wheat during the winter season (November to April), leaving the land fallow for about 60–65 days after wheat harvest until rice planting. However, sustainability of conventional RW system has recently been questioned due to the high labour, water and energy requirements (Jat *et al.* 2009; Kumar *et al.* 2013) which are gradually becoming scarce and expensive. In RW system, the soil and water requirements of the two crops are drastically different. Rice seedlings are generally transplanted in puddled and submerged soils, while wheat is planted in a well-pulverized, aerobic soil to attain potential yield. These cycles of aerobic and anaerobic conditions in the soil considerably influence CH_4 and N_2O emissions in RW system.

Nitrous oxide (N_2O) with its current concentration of 319 ppbv in the atmosphere is an important greenhouse gas (GHG) accounting for 7.9% of the total greenhouse effect (IPCC, 2007) and also responsible for the destruction of the stratospheric ozone. Of global anthropogenic emissions in 2005, agriculture accounts for about 60% of N_2O emission. Agricultural N_2O emissions have increased by nearly 17% from 1990 to 2005 (Smith *et al.*, 2007) primarily due to fertilizer N consumption, which has been increasing rapidly in the last few decades. Nitrous oxide from soil is emitted during the processes of nitrification and denitrification under alternate wetting and drying cycles in RW system. Farmers apply large amounts of nitrogenous fertilizer in RW system of IGP (Sapkota *et al*. 2014), portion of which is lost through soil N_2O emission.

The default value for N_2O emitted by N fertilizers is 1% ofthe N applied (De Klein *et al*., 2006), but the actual percentage can vary. Crutzen *et al.* (2008) reported emission factors of 3 to 5% ofthe total N applied. Lisboa *et al.* (2011), compiling data from Australia, Hawaii, and Brazil, suggested a mean emission factor of 3.9% of N applied in sugarcane fields. Emission of N_2O can be reduced by practices that deliver added N more efficiently to crops. Practices that improve N-use efficiency include using slow or controlled release fertilizer or nitrification inhibitors which slow the microbial processes leading to N_2O formation (Robertson, 2004). Akiyama *et al.* (2010) compiled data from 35 studies to evaluate CRF effects in N_2O emissions and found an overall reduction of 35% compared with conventional and organic sources of N. The N release synchronized with plant demand can increase N use efficiency and thereby reduce N_2O emissions (Hyatt *et al*., 2010; Yang *et al*., 2012). Controlled release fertilizers have small market participation because of high prices, but their importance has increased due to agronomic and environmental benefits (Chien *et al*., 2009). Nitrification inhibitors and CRFs are recognized as options of GHG mitigation. IPCC (2001) assumes an average reduction of 30% in N_2O emissions when NI and CRFs are used. However, higher reductions have been reported. Snyder *et al.* (2009) listed studies with reductions between 40 and 90% by addition of NIs to conventional fertilizers. However, the extent of the effect of NIs is not clear, especially in warm tropical soils.

The important factors effecting N_2O emission from soil are: range of oxygen concentration in soil, soil moisture content, soil texture, the amount of ammonium (NH_4^+) available for nitrification, and the amount of nitrate (NO_3^-) available for denitrification (Mosier, 1996; Granli and Bockman, 1994; Firestone, 1982). Bedard Haughn *et al.* (2006) reported that the composition of the microbial population exerts a dominant control on emissions and remains relatively constant over time, whereas interactions among spatially and temporally variable environmental drivers (NO_3- concentrations, temperature, water-filled pore space (WFPS), available carbon (C), etc.) control the magnitude of N_2O.

Emission of CH_4 and N_2O are also affected by fertilizer management and has been extensively reviewed (Linquist *et al.*, 2012). Blackmer *et al.*, (1980) reported that the amount of N_2O evolved from plots treated with $(NH_4)_2SO_4$ or urea markedly exceeded those from plots receiving the same amount of N as $Ca(NO_3)_2$. It has also been observed that N_2O emission are larger from soils fertilized with anhydrous ammonia than those of fertilizers with NO_3 and NH_4 sources (Duxbury *et al.*, 1982) and also reported that on an average, the emissions of N_2O-N induced by anhydrous NH_3 was 13 times more than that induced by aqueous ammonia or urea and represented 1.2% of anhydrous ammonia-N applied.

Urea, which is widely used nitrogenous fertilizer in the country has been reported to contribute to maximum amount of N_2O emission followed by ammonium sulphate, ammonium chloride and potassium nitrate from alluvial soil at submerged and field capacity moisture regimes (Majumdar *et al.*, 2000) and observed no unique dependence of N_2O emissions on fertilizer N application that was applied in ammonium form.

N_2O emission not only depends on the type of fertilizer N used but also on the mode of application of fertilizer N. the fertilizer derived N_2O-N losses from 250 kg N ha^{-1} of urea incorporated in the plough layer was less than (0.15%) than band application of lower rate of N applied through urea (0.27%) (Yan *et al.*, 2001). Addition of nutrients such as P and limiting materials such as $CaCO_3$ can also affect N_2O evolution from soils in some situations. Lindau *et al.* (1990) found that application of P or $CaCO_3$ increased emission of N_2O under aerobic conditions. However, P induced emissions were larger than those obtained with $CaCO_3$. Lindau *et al.* (1990) also observed that addition of $CaCO_3$ increased emissions but P addition had no effect.

3. Materials & Method

In order to achieve the objectives enshrined in the introduction, a series of laboratory and greenhouse experiments were conducted in the Division of Soil Science and Agricultural Chemistry, ICAR- Indian Agricultural Research Institute, New Delhi. Materials used and methods employed in the present investigation are briefly given below.

3.1. Laboratory experiments

3.1.1. Synthesis of nanoclay-polymer composites (NCPCs)

NCPC super absorbent was synthesized by the procedures as described by Liang and Liu (2007) by polymerization reaction with 44 ml acrylic acid which was dissolved in distilled water (10 ml) and was partially neutralized with ammonia to achieve the neutralization degree of 60% in a four-necked flask equipped with mechanical stirrer, condenser, a thermometer, and an N line. The flask was placed on a magnetic stirrer with a heating control. Then acrylamide (9.2 g), 0.264 g N, N methylene bisacrylate as cross linker, 0.642 g ammonium persulphate as initiator, and 10 wt % benitonite clay was added to the monomer solution and stirred on magnetic stirrer for 30 min until homogenous mixture was obtained. Then the temperature was increased gradually to 70 ^{o}C in presence of nitrogen gas. After completion of the polymerization reaction the resultant product was washed several times with distilled water and then dried at 100 ^{o}C to a constant weight, ground and stored for loading with urea.

3.1.2. Preparation of NCPC from sodium alginate (NaAlg)

Procedure given by Shi *et al.*, (2012) was used for the preparation of Na-Alg NCPC with slight modifications. Totally, 1 g NaAlg was dissolved in 30-mL distilled water in a 1000 mL four-necked flask equipped with mechanical stirrer, reflux condenser, gas inlet tube, and thermometer. The resultant viscous solution was stirred at 60^{o}C for 1 h and purged with N to remove the dissolved oxygen. Weighed quantity of initiator APS was added and kept at 60 ^{o}C for 15 min to generate radicals. After cooling the reactants to 40 ^{o}C, the desired amount of AA (partially neutralized), bentonite was added, the mixture was stirred vigorously for 10 min, and then MBA was added. The reaction temperature was slowly risen to 70 ^{o}C and maintained for 3 h to complete polymerization. Continuous purging of nitrogen was used throughout the reaction period. Finally, the obtained gel products were oven-dried at 70 °C to constant weight, and the dried gels were milled.

3.1.3. Preparation of NCPC from wheat flour starch

For starch based nanocomposite 10 g of wheat flour powder and 30 ml of distilled water was put in a 250-m four-necked flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line. The slurry was heated to 80 ^{0}C for 30 min under nitrogen atmosphere in the presence of initiator APS (0.32 g). After 15 min, 10 ml of AA with 60% neutralization degree (neutralized ammonia) and crosslinker MBA (0.13 g) and bentonite clay of 10% weight of AA was added. Then the temperature was increased gradually to 70°C in presence of nitrogen gas and kept for 1 h. The resulting product was washed several times with distilled water and then dried at 70 ^{0}C to a constant weight. The dried product was milled and screened.

3.2. Materials

3.2.1 Bentonite

The commercial grade bentonite (80 percentile particles were below 615 nm as obtained by using Zetatrac particle size analyzer) from Sigma Aldrich was used. The cation exchange capacity and specific surface area of the bentonite was 84 cmol (p^+) kg^{-1} and 397 m^2 g^{-1}, respectively. The small dimensions of clay particles suggest a large influence of the molecular scale behaviour and interactions (particle-particle, particle-water and interlayer) on bulk mechanical properties. The basic structural units in clays consist of the sheet formed of silica tetrahedral and the octahedral units formed of octahedral coordinated cations (with oxygens or hydroxyls) octahedral as show in Figure 3.1.

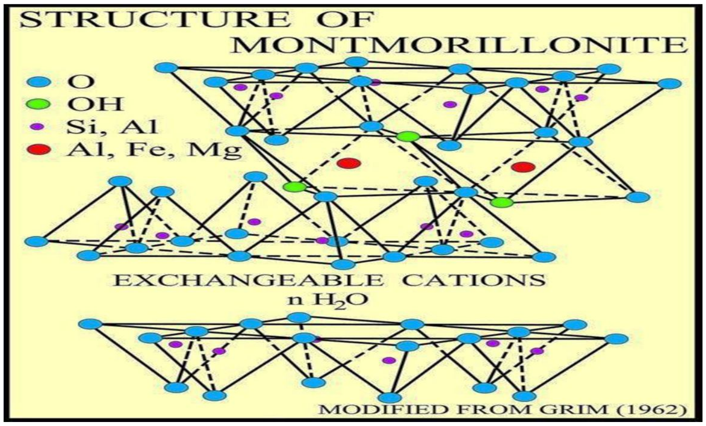

Figure 3.1: Schematic of montmorillonite structure

To advance the behavior of superabsorbent polymer composites (SPC), inorganic fillers can be used to be substitute material as research before (Li *et al.*, 2005). Clays, such as kaolin, montmorillonite, attapulgite, mica, bentonite and sercitehydrotalcite have all been used for the preparation of superabsorbent composites.

Bentonite is a naturally occurring material consisting predominantly of the clay mineral montmorillonite. Montmorillonite is a materials species in the family of sheet silicates called smectites. Smectites are three layer clays minerals. They consist of two tetrahedral layers of interconnected SiO_4 tetrahedrons which enclose a central M(O,OH)–octahedron layer (M=Al, Fe, Mg and others). The silicate layers have a slightly negative charge that is compensated by exchangeable ions in the intermediate layers. The charge is so weak that the cations (in natural form, predominantly Ca^{2+}, Mg^{2+} or Na^{+} ions) can be adsorbed with an associated hydrate shell (inner crystalline swelling).

An essential characteristic of all smectite minerals is their ability to absorb tremendous amounts of water and other liquids into their sheet structures. This gives bentonite extraordinary swelling and adhesive properties that are exploited commercially by many industries. The ability of smectite to absorb water is due in part to by the inherently small grain size of individual smectite crystals (typically much less than 2 µm) and to the fact that individual sheets possess a negative surface charge which tends to attract polar molecules. This negative charge is also responsible for another essential attribute of smectite, its ability to absorb positively charged ions from solutions, an attribute which, like adhesion, is also exploited commercially.

3.2.2 Polymer, Crosslinker and free radical initiator

Acrylic acid (AA) and Acrylamide (Am) for polymer, N,Ń-methylenebisacryamide as crosslinker and ammonium persulphate (APS) as free radical initiator, Urea extrapure AR and sodium alginate powder procured from SRL Pvt. Limited, Mumbai, India were used. Wheat flour was purchased from local market.

3.2.3. Solvents and chemicals

For routine work, GR grade chemicals and solvents were employed.

3.2.4. Loading of NCPCs with urea

he loading of urea was carried out by immersing pre-weighed dry gels into the aqueous solution of these compounds for 20 h to reach swelling equilibrium. Thereafter, the swollen gels were dried at 60 ^{o}C for 6 days. Finally the dried products were milled, screened and stored for further analysis and use.

3.3. Characterization of nanoclay-polymer composites (NCPCs)

3.3.1 Measurement of swelling behavior and kinetics

A weighted quantity of nanocomposite was immersed in distilled water at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering over a 100-mesh screen. The water absorbency Q_t (g H_2O/g sample) of the superabsorbent composite was determined by weighing the swelled samples and the Q_t of the samples was calculated using the following equation (Mo *et al.*, 2006).

$$Q_t \text{ (g } H_2O\text{/g sample)} = (m_2 - m_1) / m_1 \qquad (1)$$

Where, m_1 and m_2 are the weights of the dry sample and the water-swollen sample, respectively. Q_t was calculated as grams of water per gram of sample.

The swelling kinetics of NCPCs in distilled water was measured according to the following procedure: 1 g sample was immersed in 500 mL distilled water at set intervals (2, 4, 8, 12, 16, 20 24 and 30 hours), then swollen samples were filtered and the water absorption of NCPCs can be calculated according to Eq. (1).

3.3.2. X-Ray Diffraction technique (XRD):

X-ray diffraction is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as ‘phases’ of compound present in powder and solid samples. Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. It happens that X-rays have wavelengths on the order of a few angstroms, the same as typical inter-atomic distances in crystalline solids. That means X-rays can be diffracted from minerals which, by definition, are crystalline and have regularly repeating atomic structures. When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. In 1912, W. L. Bragg recognized a predictable relationship among several factors.

- The distance between similar atomic planes in a mineral (the interatomic spacing) which we call the d-spacing and measure in angstroms.
- The angle of diffraction which we call the theta angle and measure in degrees. For practical reasons the diffractometer measures an angle twice that of the theta angle. Not surprisingly, we call the measured angle '2-theta'.
- The wavelength of the incident X-radiation, symbolized by the Greek letter lambda and, in our case, equal to 1.54 angstroms.

$$n\lambda=2d\sin\theta$$

Where, λ- wavelength of X-ray; d-interplaner spacing; θ-diffraction angle; n-0,1,2,3….

Here X-ray diffraction analyses were carried out using a Philips PW 1710X-ray diffractometer, using APD (automated powder diffraction) software with the following setting of the instrument: Radiation type-Cu-Kα, generator voltage- 40kV, tube current-20 mA, start angle (°2θ)-3.00, end angle (°2θ) - 50.00 for clays scan step size-0.1, time per step (Sec):4.00 and type of scan: continuous. Sample holder, made up of aluminium, was cleaned with acetone solution and samples were filled in the space defined for specimen. The specimen holder was inserted in theX-ray diffractometer for the analysis.

3.3.3. Fourier transform infrared spectroscopy (FTIR)

FTIR is one of the most widely used tools for the detection of functional groups in pure compounds and mixtures and for compound comparison. Infrared (IR) study is related to the vibrational motion of atoms or molecules. In terms of frequency, the IR regions extend from 3 x 10^{12} Hz to 3 x $l0^{I4}$ Hz and in terms of wave number it extends from 100 cm^{-1} to $l0^{4}$ cm^{-1}. This study is mainly used for structure elucidation in organic and inorganic compounds. These compounds absorb electromagnetic energy in the infrared region of the spectrum. IR radiation does not have sufficient energy to cause the excitation of electrons. However, it causes atoms or group of atoms to vibrate faster about the bonds, which connect them. The compounds absorb energy from a particular region since the vibrations are quantized. The position of a particular absorption band is specified by a particular wave number.

Infrared spectroscopy of the powdered samples was carried out by using the Bruker: ALPHA, FTIR/ ATR system (24 scans, resolution- 4 cm^{-1}**)**. Clay samples were scanned in the region of 4000 - 400cm^{-1} using KBr pellets. All the spectra were recorded and analysed to know the type and nature of the functional group attachment.

3.3.4. Transmission electron microscope (TEM)

In TEM, the crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam; at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted. Modern TEMs are equipped with specimen holders that allow to tilt the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through. This produces a variation in the electron intensity that reveals information on the crystal structure. This technique, particularly sensitive to extended crystal lattice defects, is known as ‘bright field’ or ‘light field’. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen.

Transmission Electron Microscopy (TEM) was done using the instrument JEOL 100CX- 11. Solution with concentration of 1 % of each clay mineral was prepared in water and mounted on the carbon coated grid. The grid was washed with 10 drops of distilled water and then stained with 2-3 drops of 2 % uranyl acetate. After drying, the grid was examined under electron microscope.

3.3.5. Scanning electron microscope (SEM)

The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD).

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

Morphology and surface composition was determined by EVO / MA10 scanning electron microscopy (SEM) (CARL ZEISS Instrument) equipped with backscattered electron imaging (BSE), secondary electron imaging (SEI) detectors coupled with energy dispersive X-rays spectrometry (EDX). The powder samples were mounted onto double- sided carbon tape covered copper stab with industrial glue and coated by 20 nm thick palladium layers in a vacuum of 1.7 e $^{-0.005}$m bar (10^{-3}Torr) prior to analysis. The energy dispersive X-ray (EDX) analysis was simultaneously carried out to know the elemental composition of those samples.

3.3.6. Energy dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

3.3.7. Specific surface area of clay and NCPCs

Approximately 200 mg of clay and NCPCs were weighed into a tarred aluminium can, including a lid, and the sample was spread evenly over the bottom of the can.

The can, with lid beneath, was placed in a vacuum desiccators over about 250 g of P_2O_5, the desiccators was evacuated by applying a vacuum pump for one hour and dried to constant weight. Samples were wetted with approximately 2 mL of reagent-grade ethylene glycol monoethyl ether (EGME) to form clay-adsorbate slurry and placed over the CaC12 –EGME solvate. The entire culture chamber was placed in a vacuum desiccators containing $CaC1_2$. Period of 30 minutes or more was allowed for the sample- solvate slurry to equilibrate then evacuated the desiccators with a vacuum pump for about 45 minutes. The can, lid, and sample were weighed and returned to the culture chamber and the culture chamber to the desiccator. The desiccator was evacuated by applying a vacuum pump for 45 minutes. The samples were weighed at 2 to 4h intervals, evacuating between weighing, until constant weight was attained. Calculation of specific surface was done by the equation (Carter *et al.,* 1965)

$$A = Wa / (WS \text{X } 0.000286)$$

Where A = specific surface in m^2/g, Wa = weight of ethylene glycol monoethyl ether (EGME) retained by the sample in g, Ws = weight of P_2O_5-dried sample in g, and 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of surface.

3.3.8. Cation exchange capacity (CEC)

CEC of clays were determined by following procedure given by Jackson (1973). 200 mg of clay was taken in centrifuge tube; 10 ml of 0.25 M $CaCl_2$ solution was added to it and centrifuged for 10 minutes at 5000 rpm. The supernatant was decanted and the above process was repeated for another four times. Then the sample was washed two times with distilled water (10mL) followed by washing two times with 10 mL 50% acetone and two times washing with 80% acetone to remove chloride from the sample. The washing process was repeated until the sample was chloride free which was checked by treating the supernatant liquid with $AgNO_3$. The chloride free sample was added with 10 mL of 0.25 M $MgCl_2$ and centrifuged for 10 minutes at 5000 rpm. The supernatant was collected in 100 ml volumetric flask. Repeat the last step two more times and supernatant were collected. The volume was made upto 100 mL by distilled water and Ca concentration in the 100 mL supernatant was determined by AAS.

3.3.9. Release rate study of nitrogen from NCPCs in soil

The prepared NCPCs were evaluated for the release of nitrogen and nitrification inhibitory effect along with the urea as control in laboratory incubation studies. The content of $NH_4^+$and NO_3^--N were estimated by following the method given by Keeney and Nelson, (1982). 50 g of air dried, finely ground and sieved (10 mesh) soil was taken in 150 ml beakers and thoroughly mixed with the calculated amount of NCPCs having urea and nitrification inhibitors to provide 200 mg urea-N kg^{-1} soil i.e. addition of 10 mg urea-N from NCPCs in each treatment was done. The experiment was conducted in triplicate along with the concomitant controls. Distilled water was added to bring the soil moisture to one-third of the water holding capacity of soil. The content of the beaker were mixed thoroughly and incubated at room temperature in lab. The moisture content of the incubated beakers was maintained by adding the required amount of distilled water every alternate day.

3.4.1 Carbon dioxide evolution measurement

The experimental design consisted of three treatments: control (soil without NCPC), soil having AA+Am NCPC, WF NCPC and Na-Alg NCPC kept in muslin cloth. Soil controls and soil samples with test materials were prepared in triplicate. For clearer presentation, the cumulative CO_2 evolution of the soil controls was subtracted from the CO_2 evolution of the soil with test samples. Air dried soil weighing 40 g was mixed with 0.5 g of NCPCs and placed in a beaker. The moisture content of soil/soil with test material in each beaker was maintained at 55% of soil porosity. The beakers were transferred in air tight jars (500 mL capacity) to capture evolved CO_2 by NaOH trap kept in 15 ml vial inside. In decomposition study, soil respiration in-terms of amount of CO_2 monitored periodically for three months for twice in a week for the first time and once in a week for the rest of the period. Absorbed CO_2 in NaOH was precipitated as $BaCO_3$ and the excess of NaOH was back titrated with standard HCl for estimation of C mineralization in soil (Zibilske, 1994). The alkali was replaced twice in the first week period followed by once in a week for subsequent 12 weeks of incubation period. All the jars were kept inside a biochemical oxygen demand (BOD) incubator at 38 °C. A blank (without soil and with muslin cloth) was run with each set and the values of treatments were substracted from the blank value for computing CO_2- C released from each treatments. Then the CO_2-C released was expressed as mg CO_2-C g^{-1} of soil for different incubation period and fitted it into a suitable kinetics model.

3.4.2 Weight loss analysis of NCPCs

Each specimen was dug out periodically, washed with distilled water and dried to a constant weight at 60°C in an oven. The percentage of weight loss was measured using an electronic balance and calculated by using Equation (1).

$$\text{Weight loss } (W_{loss}) = \frac{W_{initial} - W_{final}}{W_{initial}} \times 100\% \qquad (1)$$

Where, $W_{initial}$ and W_{final} is the weight of sample before and after soil burial test. Three measurements were conducted for each compound.

3.5.1 Location and collection of soil samples

To accomplish the objectives of the present investigation, soil sample (0-15 cm) collected from soil type viz. Inceptisols (Typic Haplustepts) from Research Farm (28° 58′N latitude and 77° 10′E longitude with an elevation of 228.6 m above mean sea level) of IARI, New Delhi. The collected soil samples were air- dried, ground in wooden mortar and pestle, sieved to pass through 2 mm sieve and used for laboratory and greenhouse experiment studies. The salient properties of the studied soil are given in Table 3.1.

3.5.2 Determination of physical and chemical properties of soil

Soil texture

Mechanical composition of experimental soils *i.e.,* proportion of sand, silt and clay size particles were determined by hydrometer method (Bouyoucos, 1962). The texture of the soil was determined according to textural triangle proposed by USDA (Brady and Weil, 2002).

Soil pH and electrical conductivity (EC)

The pH of soil was determined in 1:2.5 (soil:water) suspension using combined electrode (glass and calomel electrodes) by digital pH meter. The EC was determined in the supernatant liquid of the same extracts with the help of conductivity bridge and expressed in dS m^{-1} at 25°C (Jackson, 1973).

Organic carbon

For determination of oxidizable organic carbon, soil samples were sieved to pass through 0.2 mm sieve. Organic carbon content in soil was determined by wet oxidation method using $K_2Cr_2O_7$ as outlined by Walkley and Black (1934).

Cation exchange capacity (CEC)

The CEC of the soil was determined by ammonium acetate method as described by Jackson (1973).

Available nitrogen (N)

Available nitrogen in soil was determined by alkaline potassium permanganate ($KMnO_4$) method as described by Subbiah and Asija (1956).

Available phosphorus (P)

For estimation of available phosphorus, soil was extracted with 0.5*M* $NaHCO_3$ (Olsen *et al.*, 1954). Phosphorus (P) content in the extracts was determined by ascorbic acid blue colour method (Watanabe and Olsen, 1965).

Available potassium (K)

Available potassium (K) was determined by extracting the soil with 1*N* ammonium acetate (pH 7.0) and K content in the extract was measured by flame photometer (Jackson, 1973).

Available Zn, Cu, Fe, Mn

For available content of zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn), soil was extracted with DTPA extractant (Lindsay and Norvell, 1978) and concentration of Zn, Cu, Fe, Mn in the extracts was determined by atomic absorption spectrophotometer.

Clay mineralogical composition of soils (by X-ray diffraction analysis)

Soils were successively treated with 30% H_2O_2 and CBD extraction (Mehra and Jackson, 1960) to remove organic matter and sesquioxides, respectively. Clays (<2 µm) were isolated from these soils following gravity sedimentation procedure (Jackson, 1956; 1976). Clay samples after the removal of organic matter and sesquioxides (cleaned clays) were used for semi-quantitative clay mineralogical analysis by XRD. These were saturated with magnesium and potassium. Expanding

		intercalation of hydrogel between the clay layers which lead to increase the d-spacing in the direction of (0 0 1) for MMT from 12.019° A to 12.351°A. In the case of Hyd/MMT/NPK, the diffraction peak related to montmorillonite is disappeared which is an indicative of exfoliated structure.	stretching vibrations), a broad band at 3418 cm^{-1} (hydroxyl groups stretching absorption), and the bands between 900 and 1200 cm^{-1} (O-C-O stretching of ether groups and -C-O stretching of alcoholic groups The peak of MMT at 1029 cm^{-1}, due to Si O group, is also observed with slight shift in Hyd/MMT and Hyd/MMT/NPK which indicates the incorporation of the MMT into the superabsorbent.	composed of more pores with open channels, as the MMT acts as physical crosslinking agent, the homogeneity as well as the pore size structure of the copolymer decreases, but the number of pores and channels increases Hyd/MMT/NPK: NPK fertilizer was homogeneously deposited on to the walls of the pores of Hyd/MMT.	
Jin *et al.*, 2013	starch/poly(acrylic acid-co-acrylamide) loaded with NP fertilizer(SAAmF)		Characteristic absorption band for starch at 3215–3558 cm^{-1}, which corresponded to the stretching vibration of O-H.	SAAmF showed the smaller three-dimensional net hole and stronger wall due to the coating	

clay minerals change their d-spacing (001) upon glycerol adsorption substantially. Therefore, glycerol salvation was employed to detect 2:1 minerals after the Mg – saturation. To differentiate between vermiculite with other minerals and to get 2nd order peaks samples treated with K were heated up to 550°C.

To achieve the semi-quantitative mineralogical composition, each sample was completely dried under vacuum for 48 h and then ground with dried potassium bromide (KBr) powder and compressed into a disc (2.5cm × 4cm). These discs were then subjected to X-ray diffraction analysis by using Cu-Kα radiation and Ni filter in a X-ray diffractometer (Model: Philips PW 1710) for measurement of integral width and full width at half maximum (FWHM) at 10 Å peak.

3.6. Greenhouse experiments

3.6.1 Test crops

Rice (*Oryza sativa*), cultivar: PB 1 was grown in 2015 during the wet or monsoon season of India (July–october). After harvest of above ground biomass (grain andstraw) of rice in October, the soils in pots were allowed to dry until wheat (*Triticum aestivum*, L.), cultivar: HD 2932 was sown in the following November and harvested in April 2016. The experiment was carried out in greenhouse at the Indian Agricultural Research Institute (IARI), New Delhi, located at 28° 37’ N latitude and 77° 9’ - 77 ° 11’ E longitudes, at an altitude of 220 m above sea level. The climate of the study area is semi-arid subtropical region.

3.6.2 Treatment combinations

Before plantation, soil of each pot was thoroughly mixed with recommended P and K fertilizers solution at 60 and 60 kg ha^{-1}. KH_2PO_4 and KCl were used as a source of P and K. A standard rate of N at120 kg ha^{-1} for rice and wheat was kept for comparison and 75 and 50% of recommended N doses were applied through urea and NCPCs along with blank (no urea) and 100% of recommended N dose through urea onlyin respective treatment pots at a depth of 2 cm from the surface. The quantities of fertilizers were estimated on the basis of percentage N content in them and the optimum value of nutrient required for plants. Three pots were used for each of NCPC, urea and control (without N-fertilizer). Details of the treatments are given below:

Treatment details:

T_1 = Control (No fertilizer)

T_2 = NPK (full dose)

T_3 = N (75% N of full dose)) + PK (full dose)

T_4 = N (50% N of full dose) + PK (full dose)

T_5 = NCPC of Wheat flour (75% N of full dose) + PK (full dose)

T_6 = NCPC of Wheat flour (50% N of full dose) + PK (full dose)

T_7 = NCPC of Sodium alginate (75% N of full dose) + PK (full dose)

T_8 = NCPC of Sodium alginate (50% N of full dose) + PK (full dose)

T_9 = NCPC (AA+AM+Clay) (75% N of full dose) + PK (full dose)

T_{10} = NCPC (AA+AM+Clay) (50% N of full dose) + PK (full dose)

3.6.3 Collection and processing of plant and soil samples

3.6.3.1 Plant samples

The rice and wheat crops were harvested at maturity. The above ground plant parts were separated into shoot and grain. The senescent leaves during crop growth were collected and pooled with the respective above ground plant parts. Plants were harvested by cutting off the stem from near ground level.

The collected plant biomass was first dried under diffused sunlight followed by oven drying at 70°C till constant dry weight was obtained. Dry weights of the shoot and grain biomass were recorded. Afterwards, plant shoots were passed through a mill to generate uniformly ground samples for further analysis. Grain samples were analyzed separately.

3.6.3.2 Soil samples

Soil samples were collected at different time interval during the entire plant growth period. After harvesting, the soils in pots were collected. Around 250 g of fresh soil was kept in deep freeze and rest of the soil was air dried in shade. These air-dried samples were ground to pass through 2 mm sieve and preserved in polythene bags for further chemical analysis.

3.7 Analytical procedures

The plant and soil samples generated from the pot culture experiment were analyzed for observation of the following parameters:

3.7.1 Plant related parameters

The following plant parameters were determined from the samples.

3.7.1.1 Growth, yield and yield components

Heights of all plants from each pot were measured in cm just before physiological maturity and means were taken. After harvesting shoots and grains were oven dried at 70°C till constant weight, and their weights were recorded separately.

At physiological maturity, the plants were harvested with a hand sickle and threshed for the aboveground biomass and grain yield determination. The sample plants were oven dried at 70°C till constant weight and weighed using a sensitive balance. Biomass yield was determined by weighting above ground dry matter of the plants (straw and grain) in each pot then grain yield was measured. Straw yield was determined as the difference between the total above ground biomass (straw + grain) and grain yield. Harvest index was computed as the ratio of grain yield to the grain plus straw yield of each pot expressed as a percentage.

3.7.1.2 Total Nitrogen content in plant

Total nitrogen content of grain and shoot samples were analysed by Kjeldahl digestion–distillation method (Buresh *et al*., 1982). Samples were digested with concentrated H_2SO_4 + digestion mixture with the help of Kjeltec digestion unit. After cooling, the contents of the tube was diluted with distilled water and distilled with 40% NaOH using Kjeltec (Kelplus-Classic DX, Pelican Instruments) semi-automatic instrument. For all the N estimations of soil and plant, the released ammonia was absorbed in 4% boric acid solution containing (methyl red+methylene blue) indicator. After that, remaining amount of boric acid was back titrated with standard H_2SO_4.

3.7.1.3Nitrogen use efficiency traits

Nitrogen use efficiency and its component traits were calculated by using the following formulas.

1) Recovery efficiency (RE) was calculated as (Dilz, 1988)

$$\text{RE}(\%) = \frac{\text{TNA in N-fertilized plot} - \text{TNA in 0 N plot}}{\text{N-fertilizer rate in N-fertilized plot}} \times 100$$

Where TNA = total N accumulation in grain and straw.

2) Physiological efficiency (PE) was calculated as (Isfan, 1990)

$$\text{PE (g grain/g N in plant)} = \frac{\text{Grain yield in N-fertilized plot} - \text{Grain yield in 0 N plot}}{\text{TNA in N-fertilized plot} - \text{TNA in 0 N plot}}$$

3) Agronomic efficiency (AE) was calculated as (Novoa and Loomis, 1981)

$$\text{AE (g grain/g N applied)} = \frac{\text{Grain yield in N-fertilized plot} - \text{Grain yield in 0 N plot}}{\text{N-fertilizer rate in N-fertilized plot}}$$

3.7.1.4. Determination of Micronutrients in Plant Samples

Micronutrients in plant samples were determined using a 9:4 mixture of HNO_3:$HClO_4$. In this method, 1 g ground plant material was placed in 100 ml volumetric flask. To this, 10 ml of acid mixture was added and the content of the flask was mixed by swirling. The flask was placed on low heat hot plate in a digestion chamber. Then, the flask was heated at higher temperature until the production of red NO_2 fumes ceases. The contents were further evaporated until the volume was reduced to about 3 to 5 ml but not to dryness. The completion of digest was confirmed when the liquid became colorless. After cooing, volume was made to

100 ml and read for micronutrients (Zn, Cu, Fe, Mn) on Atomic Absorption Spectrophotometer.

3.7.2 Soil related parameters

3.7.2.1. Sampling and estimation of ammonia and nitrate-N and determination of nitrification rate

Samples from the pot soils were drawn at 7, 14, 30, 45, 60, 75, 90 and harvest of crops. The content of $NH_4^+$and NO_3^--N were estimated by following the method given by Keeney and Nelson, (1982).For estimation of ammonium and nitrate-N 10 g dry soil was withdrawn extracted with 100 ml of 2*M* KCl solution. The content was steam distilled with NaOH using a micro-Kjeldahl distillation unit. The liberated NH_3 was absorbed in 20 ml of 2% boric acid containing mixed indicator. The distillation was continued untill 100 ml of distillate was collected within a time of 3 minutes then titrated with 0.01 *N* H_2SO_4. Nitrate N (NO_3-N) was estimated by distilling the same sample after adding Devarda's alloy (50% Cu, 45% Al and 5% Zn). After removal of NH_4^+-N from the sample as described above, distillation was done by adding 0.25 g Devarda's alloy powder into the flask. The NO_3^--N liberated during second distillation was absorbed in another conical flask containing 20 mL of 2% boric acid solution mixed with mixed indicator. The content was then titrated against 0.01 *N* H_2SO_4.

Determination of nitrification rate of different fertilizer treatments

The content of NH_4^+ and NO_3^- - N were estimated by following the method given by Keeney and Nelson, (1982). NO_2^- -N was estimated by following the modified Greiss-Ilosvay method (Keeney and Nelson in 1982). The nitrification rate and percentage nitrification inhibition were calculated as per Sahrawat, (1980) as follows:

$$\text{Nitrification rate} = \frac{(NO_3^- + NO_2^-) - N}{(NH_4^+ + NO_3^- + NO_2^-) - N} \times 100$$

3.7.2.2. Determination of Total N in Soil

Total N in soil samples was determined by the Kjeldhal method of Bremner (1996). In this method, 0.25 to 0.50 g of finely ground soil sample was digested with 3 to 6 ml of concentrated H_2SO_4 in the presence of digestion mixture containing K_2SO_4, $CuSO_4$ and Se (100:10:1) on block digester for about 4-5 hours. After cooling, the digest was distilled with 20 to 40 ml of 40% NaOH solution into 10 ml boric acid mixed indicator solution. The distillate was titrated against 0.1 *N* HCl solutions and the amount of N calculated as 1 ml of 1 *N* HCl equals 14 mg N.

3.7.2.3. Determination of Organic C in Soil

Total organic C in soil samples was determined by the Walkley-Black procedure. In this method, 1.0 g of finely ground soil sample was treated with 10 ml of 0.167 *M* (1 *N*) $K_2Cr_2O_7$ solution in the presence of 20 ml concentrated H_2SO_4 to completely oxidize organic C. After 30 min, 200 ml water was added and the suspension was filtered using an acid resistant filter paper (e.g., Whatman 540). The filtrate was titrated against 0.5 *M* (0.5 *N*) $FeSO_4.(NH_4)_2SO_4$in the presence of *o*-phenanthroline indicator. Also made a blank determination in the same manner, but without soil, to standardize the $K_2Cr_2O_7$. The amount of organic C was determined from the amount of $FeSO_4$. $(NH_4)_2SO_4$ used in the titration of blank and sample using the following formula:

$$\text{Organic C (\%)} = \frac{10\,(B-T)}{B} \times \frac{0.003 \times 100}{\text{wt. of soil (g)}}$$

Where B = volume (ml) of $FeSO_4$. $(NH_4)_2\ SO_4$ solutions required for blank titration.

T = volume (ml) of $FeSO_4$. $(NH_4)_2\ SO_4$ solutions required for titration of soil sample

3.7.2.4. Microbial biomass carbon (MBC)

MBC in soil was analysed by the procedure given by Jenkinson and Powlson (1976). Three sets of 10 g fresh soil were taken in beakers, the first one was fumigated with chloroform for 24 hours, while the second one was kept unfumigated, and the third one was kept for the determination of moisture. Both the fumigated and unfumigated soil samples were extracted using 0.5M potassium sulphate (K_2SO_4). Small amount of extract was digested with potassium persulphate ($K_2S_2O_8$) at 120°C for 2 hours in a digestion block. The carbon dioxide evolved during the digestion was trapped in 0.1N sodium hydroxide (NaOH) taken in a vial kept over the constriction inside the digestion tube. A control was also run using 0.5M potassium sulphate K_2SO_4 in place of the extract. The unconsumed NaOH was determined by titration with standard 0.01N sulphuric acid (H_2SO_4) using phenolphthalein indicator. The MBC was calculated using the formula given below and reported on oven dry soil basis.

$$\text{MBC (mg kg}^{-1}\text{)} = (C_F - C_{UF}) / K_{EC}$$

Where,

C_F - Carbon in fumigated soil

C_{UF} - Carbon in unfumigated soil

K_{EC} - Efficiency of extraction (0.25)

3.7.2.5. Microbial biomass nitrogen (MBN)

The microbial biomass nitrogen in the soil was estimated by fumigation extraction method as outlined by Brookes *et al.* (1985). Moist sample was taken in duplicate (to give approximately 20 g oven dry weight) in 100 ml. glass beakers. One set was kept inside a vacuum desiccator and fumigated as described in case of microbial biomass carbon (Jenkinson and Powlson, 1976). The fumigated and non-fumigated soils were extracted with 0.5M K_2SO_4 (1:4 Soil:Solution ratio) and nitrogen content of the extracts were determined by following the modified procedure of Brookes *et al.*, (1985) in which 40 ml. of the extract was taken and total N was measured after digestion. One ml. of $CuSO_4$ solution (0.19 M) and concentrated H_2SO_4 (10 ml.) were added to the extract in 250 ml. capacity digestion tube and mixture was refluxed for 2 hours. After cooling, double distilled water was added to the digestion tube. The content of the tube was steam distilled with 40% NaOH to trap the evolved NH_3 into boric acid and mixed indicator solution using Kjeltech semi-automatic distillation unit. The distillation was continued until 100 ml. of distillate has been collected, and then it was titrated with 0.01 N H_2SO_4. The MBN was calculated as follows:

$$\text{MBN (mg kg}^{-1}) = (ON_F - ON_{UF}) / K_{EC}$$

Where,

ON_F - Organic nitrogen in fumigated soil

ON_{UF} - Organic nitrogen in unfumigated soil

K_{EC} - Efficiency of extraction (0.25) as per Bremner and Kessel (1990)

3.7.2.6. Dehydrogenase activity

Dehydrogenase activity in soil was determined by estimating the rate of production of tri- phenyl formazan (TPF) from tri-phenyl tetrazolium chloride (TTC). The method of Klein *et al.* (1971) was followed for the assay of dehydrogenase activity as outlined below.

Briefly 1 g soil was placed in 15 ml screw capped tube. To this 0.2 ml of 3% TTC and 0.5 ml of 1% glucose were added and ensured to make the system anaerobic, the tubes were incubated at 28 °C for 24. After incubation 10 ml of methanol was added and shaken for exactly one minute. It was allowed to stand in dark for six hours. The color intensity developed, was measured at 485 nm (blue filter). From the standard curve, drawn in the range of 0.004 to 0.4 mg TPF per 10 ml of methanol, the TPF produced in the samples were computed. Dehydrogenase activity was expressed as TPF formed per gram soil for 24 hours on oven dry weight basis.

3.7.2.7. Phosphatase activity

To one gram of soil in a 50 ml conical flask, 4 ml of modified universal buffer (pH 6.5 for acid phosphatase and pH 11 for alkaline phosphatase), 1 ml of *p*-nitro phenyl phosphate were added and incubated for one hour at 37 °C. After incubation 4 ml of 0.5 M NaOH and 1 ml of 0.5M $CaCl_2$ were added and the contents filtered the amount of *p*-nitro phenol (PNP) present in the filtrate was measured colorimetrically at 440 nm. The phosphatase activity was calculated after deducting the PNP formed in the control (where no *p*-nitro phenyl phosphate was added), from the PNP produced in the samples. The results were expressed as PNP g^{-1} h^{-1} (Tabatabai and Bremner, 1969).

3.7.2.8Urease activity

Urease activity was determined following the method described by Douglas and Bremner (1971). Briefly, 5 g of soil was transferred to 125 ml polypropylene bottles and incubated at 37 ºC for 5 h after addition of 250 ppm urea solution. At the end of the incubation, urease activity was stopped by adding 2M KCl-PMA solution to soil sample followed by shaking the contents for 1 h and filtration trough Whatman No. 1 filter paper. The amount of urea unhydrolyzed was determined by colorimetric procedure as described by Douglas and Bremner (1971). Soil ureas activity (µg urea g^{-1} soil h^{-1}) was calculated by the formula given below:

$$\text{Urease activity} = (B-A)/t$$

Where, B =amount of urea N at 0 h, A = amount of urea N founded after time (t) i.e. 5 h.

3.8. Greenhouse gas sampling and analysis

Closed chamber technique was adopted for the collection and sampling of N_2O (Pathak *et al.*, 2002). Chamber of dimension 30 cm x 30 cm x 100 cm (length x width x height) made of 6 mm thick acrylic sheets and fitted with a battery operated fan, a thermometer and a three way stopcock at top were used for this purpose (Figure 3.2). An aluminium channel was placed in the field and used with each acrylic chamber. The aluminium channel was inserted 10 cm inside the soil and the channels were filled with water to make the system air tight. Three channels were randomly fixed in each treatment plot to take gas samples in triplicate. Gas sampling was carried out between 9:00 and 10:30 A.M. from all the pots once in a week and 3 days after fertilizer application for continuously 3 days up to 60 days of the crop period. Gas samples were drawn with 50 ml syringe with the help of a hypodermic needle at 0, 30, and 60 min and syringe were made air-tight with a three-way stopcock and analysed for determination of N_2O concentration within 72 hours of sampling. Head space volume inside the box was recorded, which was used to calculate flux of N_2O. Concentrations of N_2O gas samples from rice and wheat pots were analysed using Gas Chromatographs (GC: Hewlett Packard 5890 Series II) fitted with electron capture detector (ECD), flame ionization detector (FID) and 6’ x 1/8” stainless steel column (Porapak N). The carrier gas was N_2 with a flow rate of 14 ml min^{-1}. N_2O concentration was estimated by GC-ECD with 50, 120, and 350 °C column, injector, and detector temperatures, respectively. The standards of N_2O were obtained from Spectra Gases, USA. Estimation of total N_2O emission during the crop season was done by successive linear interpolation of average emissions of N_2O on the sampling days assuming that N_2O emissions followed a linear trend during the periods when no sample was taken.

Calculation of N_2O gas flux

The following formula was used to calculate the flux

Cross sectional area of the chamber = A m^2

Headspace = H m

Volume of headspace = AHm^3 = 1000 x AH liter

N_2O Concentration at 0 time = Co ppbv

N_2O Concentration in time t = Ct

Change in Concentration in time t = (Ct – Co) ppbv

= (Ct –Co) µl l^{-1}

Volume of N_2O evolved in time t = (Ct –Co) µl l^{-1} x 1000 AH liter

= (Ct –Co) x AH µl

When t is in hours, then flux is F = [(Ct –Co) x AH)/ (A x t) µl m-2 h^{-1}

Now 22.4 µl of N_2O is 44 µg at STP

So, Y µl of N_2O is (44 x Y/22.4) µg at STP

Therefore, Flux = Y x 44/22.4 µg m-2 h^{-1}

Hence, Flux = [Ct – Co/t] x H x 44/22.4µg m^{-2} h^{-1}

			The peak observed at 2930.25 cm^{-1} in starch corresponded to the stretching vibration of saturated C-H groups, which shifted from 2930.25 to 2872.40 cm^{-1} in the composite due to the addition of grafting polymer chains.	polymer with 40 wt % starch. Whereas, the larger net hole of the coating polymer with 15 wt % starch were observed.	
Rashidzadeh *et al.*, 2014	Sodium alginate, acrylic acid, acrylamide, and clinoptilolite (NaAlg–g–p(AA–co–AAm)/Clin)	The diffraction peaks appeared at 2θ=9.85°, 11.19° and 22.4° corresponding to the clinoptilolite. These peaks were also found in NaAlg–g–p(AA–co–AAm)/Clin, confirmed the presence of clinoptilolite in the nanocomposite composition	**Clinoptilolite**: peak at 3449 cm-1 due to the OH stretching vibration in (Al–OH–Al) and (Si–OH–Si) of. peaks at 1638 cm^{-1} and 1080 cm^{-1}are related to the H–O–H bending and Si–O(Si),(Al) stretching vibrations, respectively. **NaAlg:** 1640 cm^{-1} and 1419 cm^{-1} wave numbers, which are due to the carboxylate stretching vibrations. The broad band at 3418 cm^{-1} is due to the stretching absorption of the hydroxyl groups of the polysaccharide.	porous structure of hydrogel of size several tens of microns hydrogel nanocomposite is composed of larger-sized open pores with interconnected rooms inside,	

So, for one hectare/day N_2O

$$\text{Flux} = \frac{[Ct - Co/t] \times H \times 44/22.4 \times 10000 \times 24 \text{ mg}}{1000}$$

$$N_2O - N \text{ flux (mg ha}^{-1}\text{d}^{-1}) = \frac{[Ct - Co/t] \times H \times 44 \times 240 \times 28}{22.4 \times 44}$$

$$= [Ct - Co/t] \times 300\text{mg ha}^{-1}\text{d}^{-1}$$

3.9. Statistical Analysis

The data obtained from the pot experiments and incubation study was subjected to analysis of variance appropriate to the experimental design. The means of all the treatments were separated by using DMRT (Gomez and Gomez, 1984) at 5% level of significance and as per standard ANOVA. Pearson’s correlation matrix was also computed. All the data were statistically analyzed following computer package SPSS 21.

4. Results

4.1. Physico-chemical properties of the soil

The bulk surface soil samples (0-15 cm), collected from Inceptisols (Typic Haplustepts) from the Research Farm of ICAR-Indian Agricultural Research Institute (IARI), New Delhi and used in the present investigation. The physical and chemical characteristics of these soils are described in Table 4.1.

4.1 Results

4.1.1 Infrared spectroscopy (FTIR)

The FTIR spectra of (a) Urea, (b) Bentonite, (c) Wheat Flour (WF) powder, (d) Na-Alg powder, (e) AA+Am NCPC, (f) WF NCPC and (g) Na-Alg NCPC were shown in figure 4.1- 4.7 and the same are enumerated in table 4.2. The characteristic peaks at 1032 cm^{-1} due to the Si-O stretching, and 912, 3619, and 3442 cm^{-1} due to the -OH group were found in the commercial bentonite sample (Figure 4.2). After the formation of nanocomposites the two absorption peaks (912, 3619 cm^{-1}) of -OH group of bentonite disappeared due to polymerization (Figure 4.5, 4.6 and 4.7).

The FTIR spectrum of the urea (Figure 4.1) showed the characteristic carbonyl peak at 1671 cm^{-1} (C=O), and two N-H absorbency bands at 3427 and 3326 cm^{-1}.In the IR spectrum of Na-Alg (Figure 4.4), the broad peak which was present between 3000-3400cm^{-1} is characterized as the H-bonded O–H stretching frequency.The band at approximately 2911 cm^{-1} is assigned to C–H stretching. Although the fingerprint region (1000 – 750 cm^{-1}) is seldom looked into in detail by researchers, it is the most discussed region in carbohydrates.The peaks at 1300, 1020 and 947 cm^{-1} are all due to stretching vibrations of C–O from glycosidic bonds, with the stretching vibration of C–O–C from glycosidic bonds contributes to the peak at 947 cm^{-1} as well. In addition, there are two peaks at 1592 and 1397 cm^{-1} indicating the COO^{-} stretching group attached to the sodium ion.The former is caused by the asymmetric stretching vibration of the carboxylate COO^{-}while the latter is deduced to be due to C–OH deformation vibration with contribution of COO^{-} symmetric stretching vibration of the carboxylate group.

The characteristic absorption band of Na-Alg (Figure 4.4) at 1020 cm^{-1} (stretching vibration of C─OH groups) was weakened after reaction.In FT-IR spectra of

Na-Alg NCPC (Figure 4.7), the bands at 1683 cm^{-1} is related to the stretching vibration of the carbonyl groups of AA. It was observed that the absorption bands of carbonyl at 1673 cm^{-1} in both AA+Am NCPC and WF NCPC and at 1683 cm^{-1} in Na-Alg NCPC might be due to the formation of hydrogen bonding between the carboxyl and carbonyl groups of the hydrogel materials and the hydroxyl groups of Al-OH and Si-OH in bentonite.

The infrared spectrum of starch showed a characteristic absorption band at 3275–3655 cm^{-1} (Figure 4.3), which corresponded to the stretching vibration of O-H (carbons 2, 3, and 6). The band became sharper, and there was a shift from 3275 to 3253 cm^{-1} (Figure 4.6), and a negative shift from 3655 to about 3429 cm^{-1} was observed, as shown in Figure 4.6. The peak observed at 2921 cm^{-1} (Figure 4.3) corresponded to the stretching vibration of saturated C─H groups, which shifted from 2921 to 2897 cm^{-1} (Figure 4.6). The characteristics for the saccharide structure of starch were appearing at 1647 and 1148 cm^{-1}, as shown in Figure 4.3, which could be assigned to symmetric and asymmetric stretching vibrations of the C─O─C bridge, respectively. It was evident that a stronger and wider peak appearing at about 1673 cm^{-1}, shown in Figure 4.6, was due to the symmetric stretching vibration of the C─O─C bridge.

The peak of bentonite at 1032.83 cm^{-1}, due to Si-O group, is also observed with slight shift to 1062 cm^{-1} in Na-Alg NCPC, whereas very weak peak was observed in both AA+Am and WF NCPCs indicates the incorporation of the bentonite into the superabsorbent.

4.1.2 X-ray diffraction (XRD) analysis

The XRD was used to confirm the mineralogy of the bentonite clay and polymerization of NCPCs. XRD patterns of the commercial bentonite clay (SSA 396.74 m^2g^{-1} and CEC 83.95 (cmol ($p^{+)}$ Kg^{-1})) confirmed the presence of montmorillonite as a major phase because, the peak at 2θ=6.8 (d spacing =13.01 Å) corresponds to smectite (2:1 mineral) (Figure 4.8, 4.9 and 4.10). The XRD pattern of AA+Am NCPC, WF NCPC and Na-Alg NCPC did not show the characteristic basal peak of bentonite particles after their incorporation into the polymer matrix (Figure 4.8, 4.9 and 4.10). crystalline nature of sodium alginate powder can be seen as diffraction peaks observed at 21.5 and 39 degree2θmay be assigned to the reflection of their (2 0 0) plane from the polymannuronate, and others from amorphous halo

Sarkar *et al*., 2014	Partially neutralized acrylic acid and acryl amide with different types of nanoclays (10 wt %) (NCPC) Clay I: kaolinite Clay II: mica Clay III: smectite	Clay I was dominant in kaolinite (80%) as indicated by the presence of a peak around a 2θ of 12.4°. Clay II was dominant in mica (70%), which was indicated by the presence of a peak at a 2θ of 8.8°. clay III was dominant in smectite (60%), which was indicated by the presence of a peak at a 2θ of 5°	The absorption bands in the range 3400–3700 cm^{-1} were attributed to the stretching of –OH. The vibration bands observed for different clays at 1035, 1035, 1031, 1032, 1028, and 1029 cm^{-1} were due to Si-O stretching. The disappearance of the absorption bands of the A-H stretching of various clays in the range 3400–3700 cm^{-1} and the weakening of the absorption bands at about 1030 cm^{-1}, due to Si-O of clays, took place after the incorporation of various clays into the polymer network.		Platy morphology of the clays, their length and width, remained parallel to the horizontal and were viewed in the plates. The approximate thicknesses of clays I, II, and III were calculated and found to be 8.75, 10, and 5 nm, respectively; these were close to the values obtained from XRD, except for kaolinite.

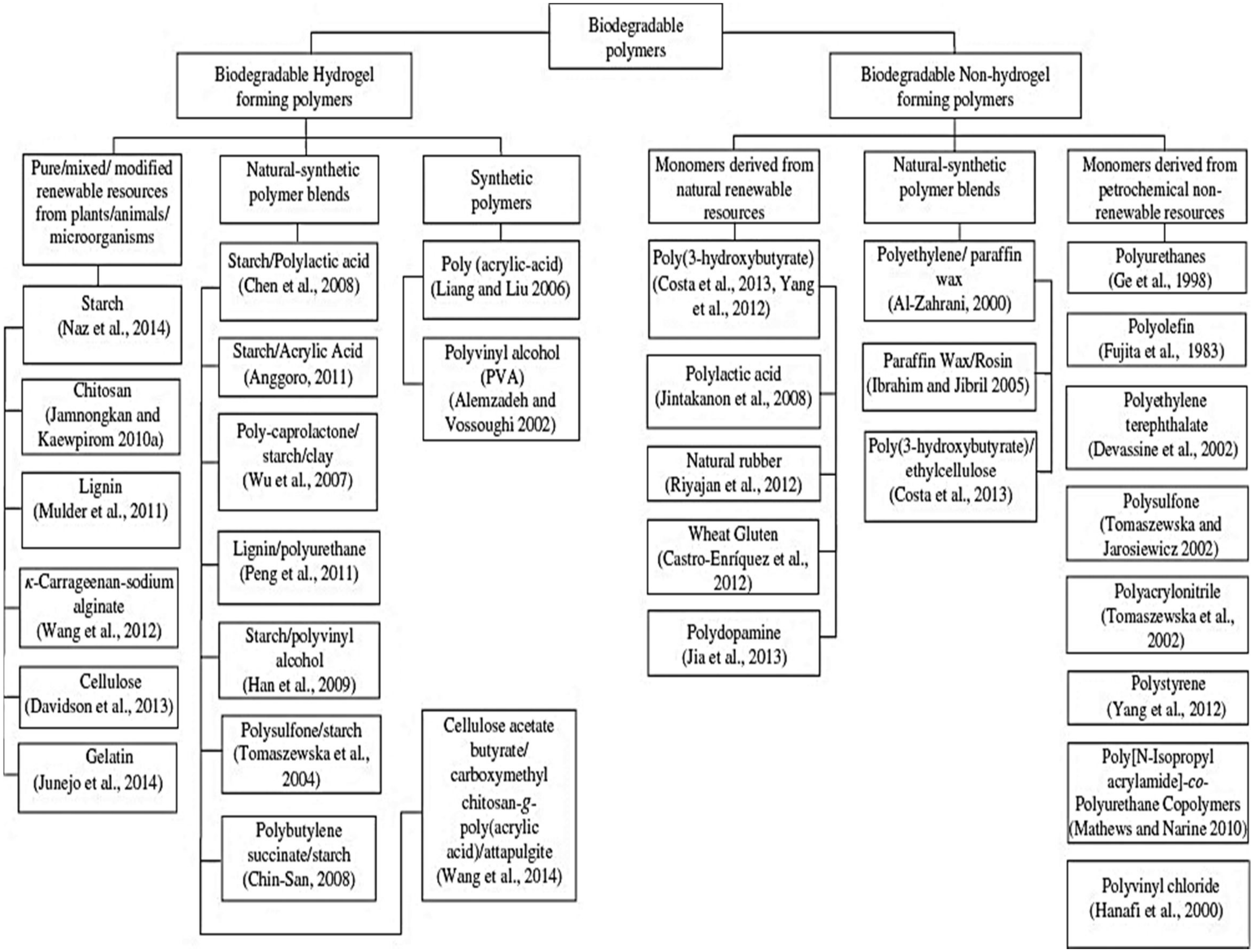

Figure 2.1 Classification of biodegradable polymers and their blends reported in the literature (Majeed *et al.*, 2015)

Table 3.1 Some important physico-chemical properties of the soil used in the present investigation

Parameters	**Inceptisol (IARI)**
$pH_{1:2.5}$	8.11
$EC_{1:2.5}$ (dS m^{-1})	0.28
Mechanical composition	
Clay (%)	15.5
Silt (%)	20.2
Sand (%)	64.3
Textural class	Sandy loam
Organic C (%)	0.39
CEC [cmol(p^+)Kg^{-1}]	11.7
Available N (kg ha^{-1})	227
Available P (kg ha^{-1})	27.32
Available K (kg ha^{-1})	350.2
Available Zn (mg kg^{-1})	1.53
Available Cu (mg kg^{-1})	1.50
Available Fe (mg kg^{-1})	3.80
Available Mn (mg kg^{-1})	8.50

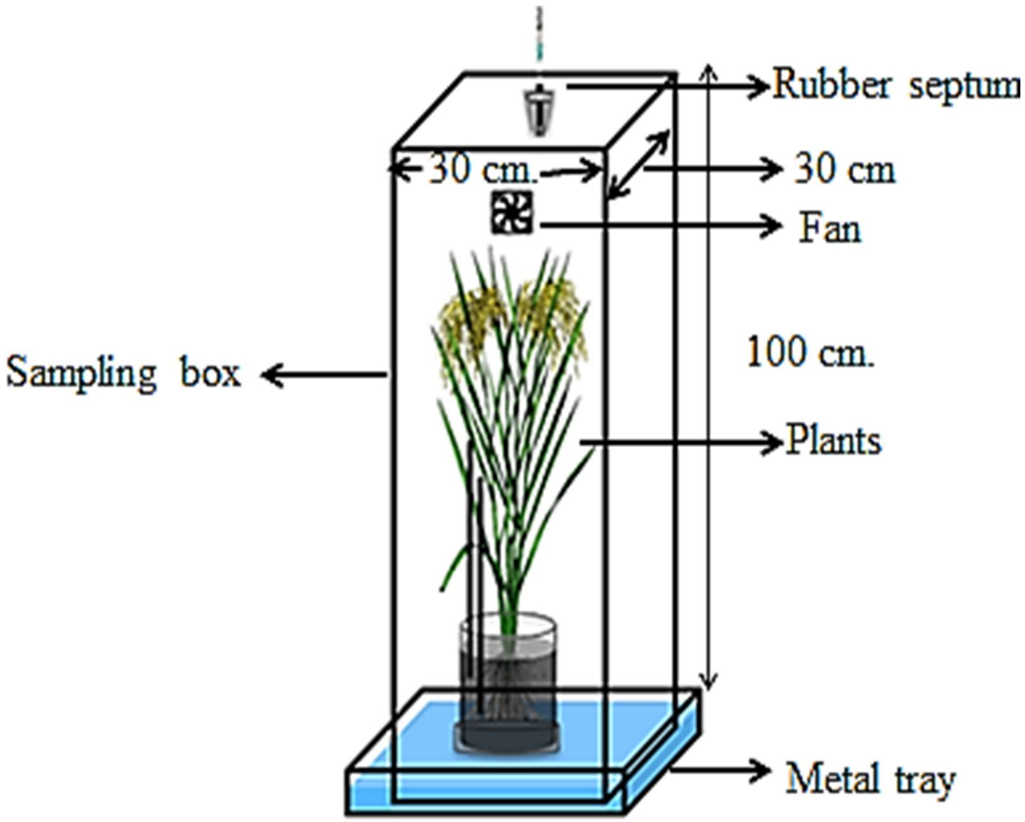

Figure 3.2 closed chamber used for N_2O sampling

Table 4.1 Some important physico-chemical properties of the soil used in the present investigation

Parameters	**Inceptisol (IARI)**
$pH_{1:2.5}$	8.11
EC $_{1:2.5}$ (dS m^{-1})	0.28
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Sand (%)	64.3
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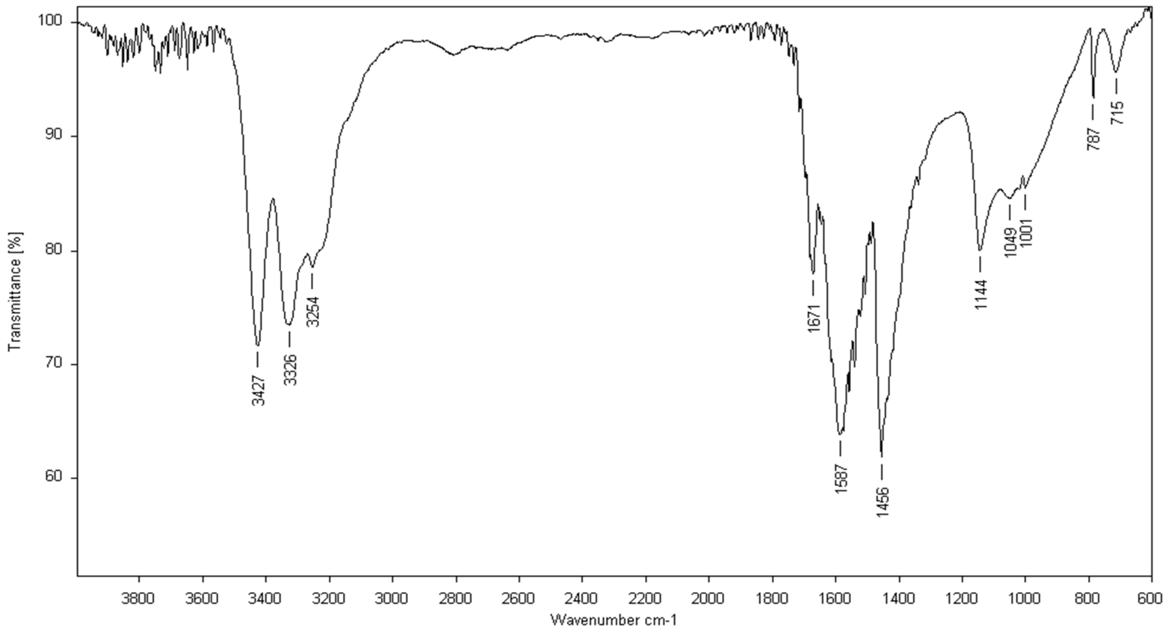
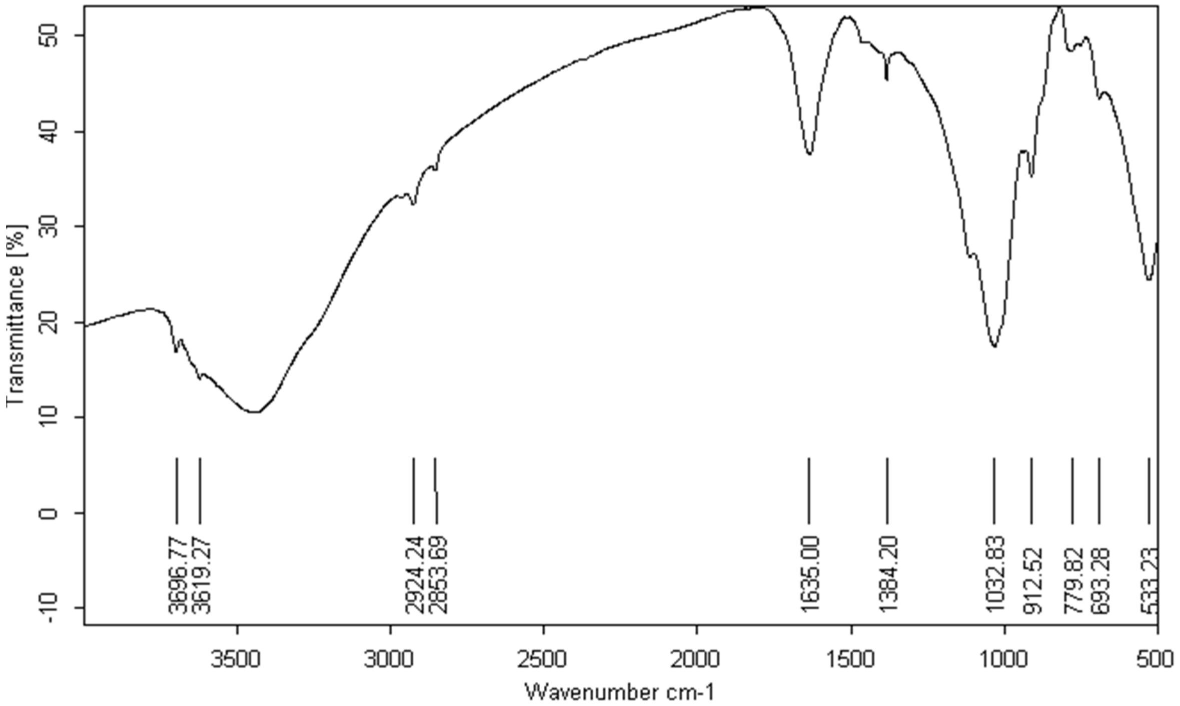
Organic C (%)	0.39
CEC [cmol(p^+)Kg^{-1}]	11.7
Available N (kg ha^{-1})	227
Available P (kg ha^{-1})	27.32
Available K (kg ha^{-1})	350.2
Available Zn (mg kg^{-1})	1.53
Available Cu (mg kg^{-1})	1.50
Available Fe (mg kg^{-1})	3.80
Available Mn (mg kg^{-1})	8.50



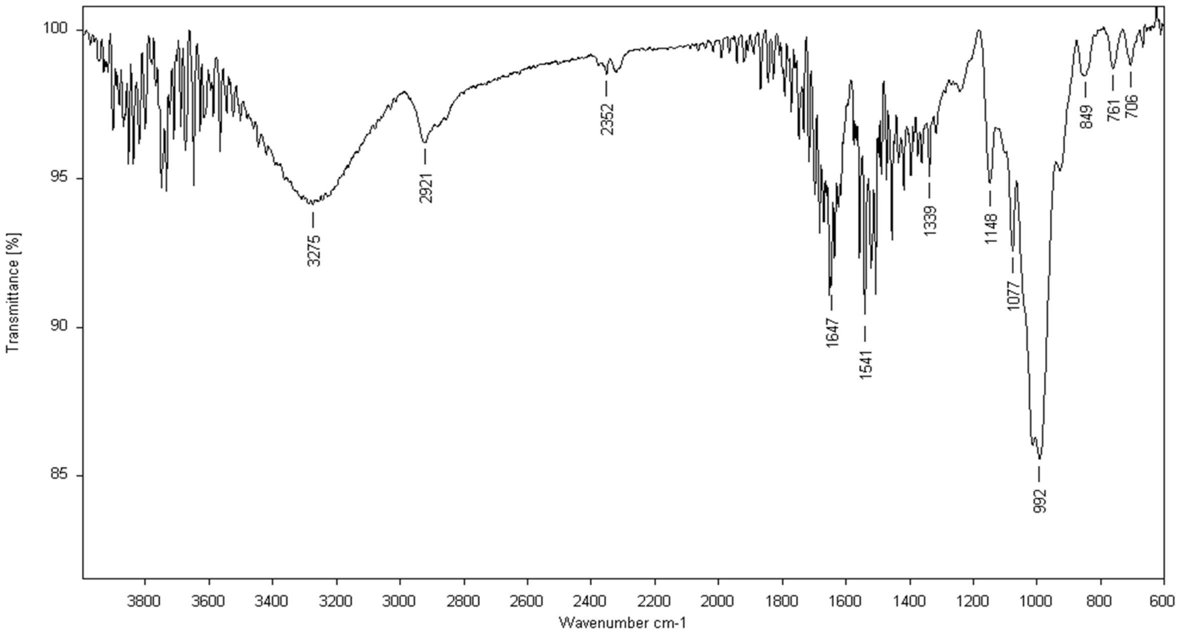
Urea

Figure 4.1 FTIR spectra of urea



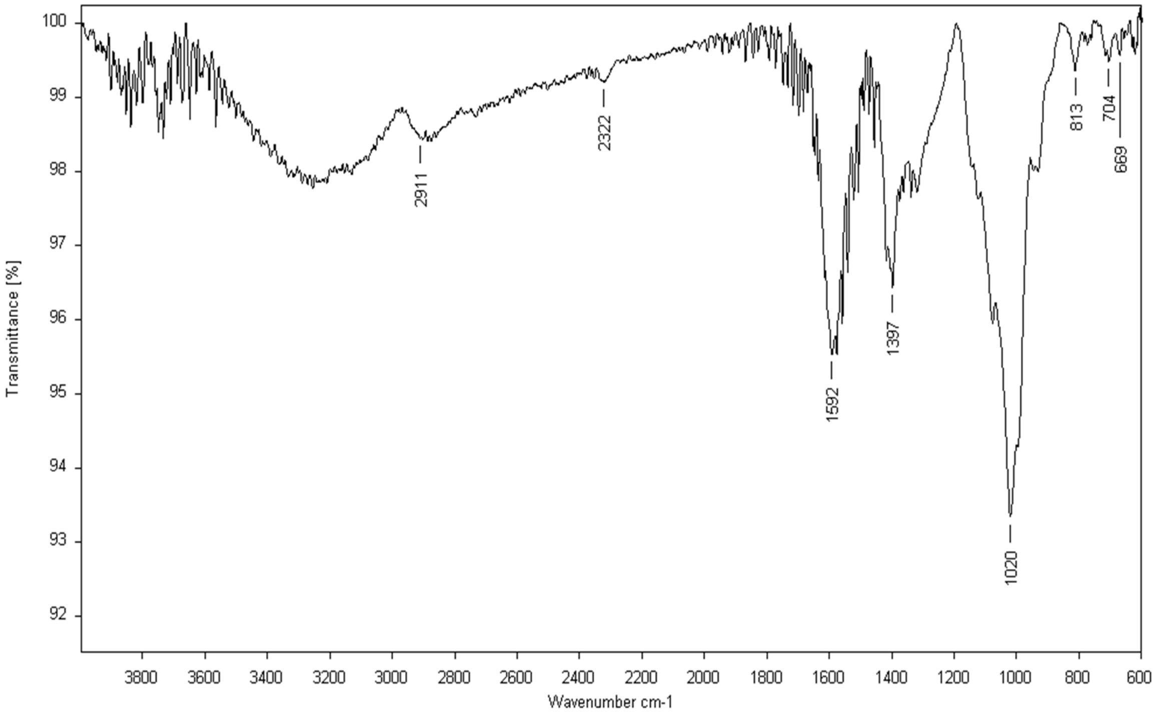
Bentonite

Figure 4.2 FTIR spectra of commercial bentonite



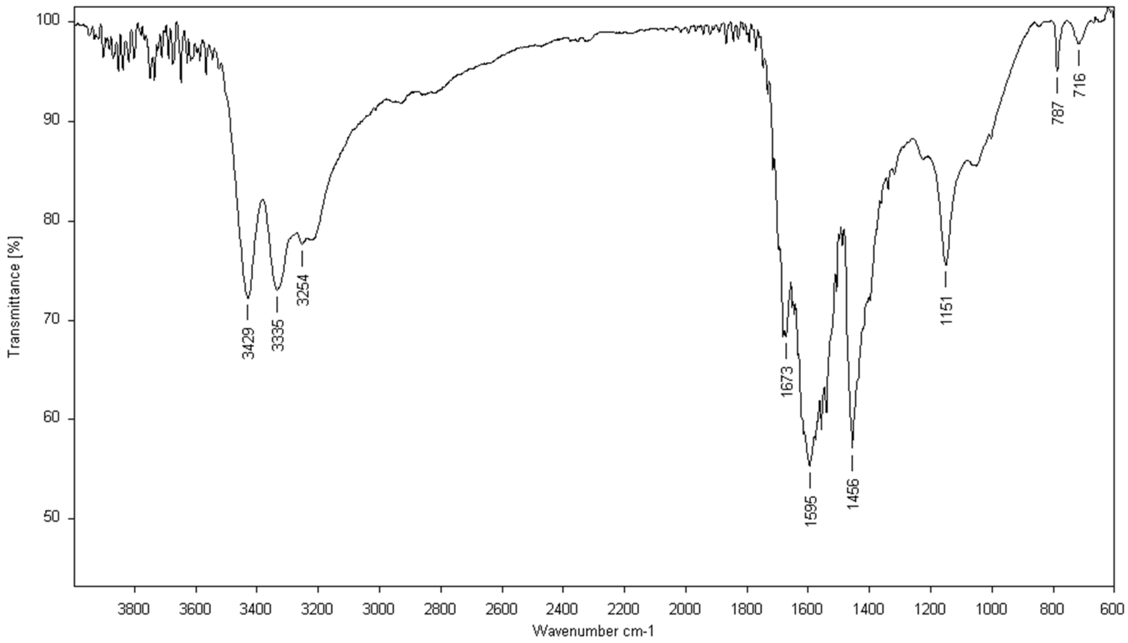
WF powder

Figure 4.3 FTIR spectra of WF powder



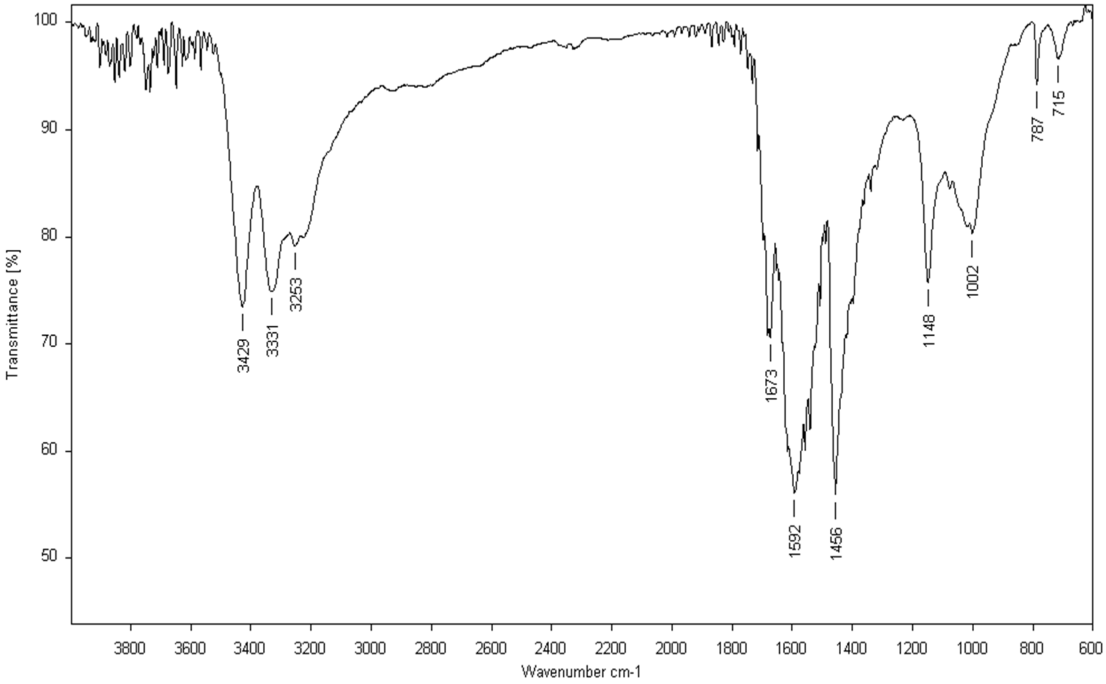
Na-Alg powder

Figure 4.4 FTIR spectra of Na-Alg powder



AA+Am NCPC

Figure 4.5 FTIR spectra of AA+Am NCPC



WF NCPC

Figure 4.6 FTIR spectra of WF NCPC

(Figure 4.11). The XRD spectra of urea powder showed its crystalline nature which was quite clear from the occurrence of sharp peaks at specific Bragg's angles (Figure 4.8, 4.9 and 4.10).

4.1.3 Transmission electron microscopy (TEM)

TEM observation of the images showed the flaky and plate-like bentonite clay particles with pseudo–hexagonal morphology. Particle size ranged from 15.08 to 36.96 nm (Plate No. 4.1a). The black spots seemed to indicate particle aggregation. The nano-scale bentonite hexagonal particles were also observed in the TEM images of AA+Am, WF and Na-Alg NCPC, which were almost embedded within the polymer matrix (Plate No. 4.1b,c and d).

4.1.4 Scanning electron microscopy (SEM)

We can clearly see the plate like structure exhibited by bentonite in the SEM image (Plate No. 4.2 a) as leafy, lamella like structures with several pores. SEM micrograph of WF NCPC showed highly porous and honeycomb like structure with highly dispersed clay particles as compared to AA+Am and Na-Alg NCPCs (Plate No. 4.2 b, c and d). Further it could be seen that the surface of NCPCs made with sodium alginate was having more number of pores with open channel than others (Plate No. 4.2 d). AA+Am NCPCs (Plate No. 4.2 b) displayed the rough and loose surface with uniformly incorporated bentonite clay in the polymer matrix and enhanced the water uptake capacity of the nanocomposites.

4.1.5 Scanning electron microscopy energy dispersive X-ray (SEM-EDX)

In addition from the SEM images, EDX spectra of the bentonite, AA+Am, WF and Na-Alg NCPCs were collected to evaluate their elemental composition. The EDX spectra of the regions correspond to polymer-intercalated bentonite, showed significant amounts of Si and Al (clay constituents). The weight percentage of Si and Al in AA+Am was 1.33, 0.66, in WF NCPC was 1.31 and 0.56 and in Na-Alg NCPC was found as 1.30 and 3.82 (Table 4.3). The SEM-EDX analysis also confirmed the redispersed crystals of urea in NCPCs with predominant amount of N, C and O, that is, urea constituents.

4.1.6 Water absorption and swelling kinetics in water by NCPCs

The observed trends in the swelling kinetics for all the NCPC samples are very similar. Initially, the rate of water uptake sharply increases, followed by a slower rate until the equilibrium is reached. It was observed that the synthesized NCPCs reached their equilibrium swelling values after 24 hours (Figure 4.12a). The equilibrium water absorbance by the AA+Am, WF and Na-Alg NCPC were 68.5, 54.3 and 81.9 g/g respectively (Figure 4.12a).

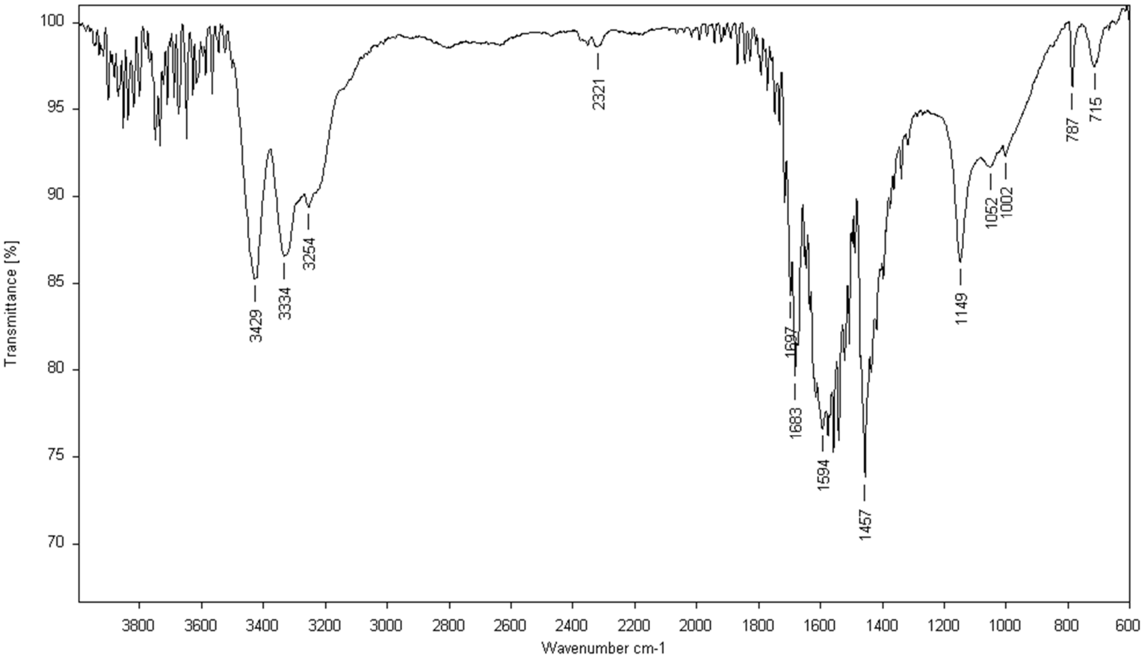
Figure 5b represents the swelling kinetic curves of AA+Am, WF and Na-alg NCPC in distilled water. It can be seen that the swelling rate of the nanocomposites is faster within 4 hours and then increase gradually. In this section, the swelling kinetics can be expressed by Schott's pseudo second order kinetics model (Eq. (2)) (Schott, 1992).

$$t/Q_t = 1/K_{is} + (1/Q_\infty)\ t \tag{2}$$

Q_t is the water absorption at a given swelling time t (s); Q_∞ (g/g) is the power parameter, denoting the theoretical equilibrium water absorption; K_{is} the initial swelling rate constant (g/g s). As shown in Figure 4.12b, the plots of t/Qt versus t gave a perfect straight line with good linear correlation coefficient of 0.9877, 0.9925 and 0.9937 for WF, AA+Am and Na-Alg NCPC respectively, which indicates that the swelling behaviors of the nanocomposites follow the pseudo second order model. By fitting experimental data using Eq. (2), the values of Q_∞ and K_{is} can be calculated through the slope and intercept of the above lines. The K_{is} values are 0.003, 0.006 and 0.007 g/g s, and the Q_∞ values are 69.44, 79.37 and 95.24 g/g in distilled water for WF, AA+Am and Na-Alg NCPC, respectively. It can be concluded that the swelling capacity and swelling rate of Na-Alg NCPC was higher than AA+Am and WF NCPC in distilled water.

4.1.7 Nitrogen release behavior of NCPCs in soil

The nitrogen content of WF, AA+AM and Na-Alg NCPC after urea loading was 19.10, 24.13% and 26.07%, respectively.The release of NH_4^+-N content decreased gradually during the 30 days of incubation period (Figure 4.13a), under soil conditions. The ranges of NH_4^+-N content were significantly high in all NCPCs as compared to urea alone. Among the all NCPCs, Na-Alg NCPC showed the higher NH_4^+-N concentration which was 46.64, 34.82, 26.74 and 20.35 mg kg^{-1} of soil at 2,



Na-Alg NCPC

Figure 4.7 FTIR spectra of Na-Alg NCPC

Table 4.2 FTIR peaks of bentonites, urea, WF powder, Na-Alg powder, acrylamide, AA+Am NCPC, WF NCPC and Na-Alg NCPC before and after degradation.

Sample	**FTIR peaks (cm^{-1})**
Commercial bentonite	3696.77, 3619.77, 3442, 2924.24, 2853.69, 1635, 1384, 1032.83, 912.52, 779.82, 693.28
Urea	3427, 3326 3254, 2473, 2327, 2012, 1671, 1625, 1587, 1456, 1144, 1049, 1001, 787, 715
WF powder	3275, 2921, 2352, 1647, 1541, 1339, 1148, 1077, 992, 849, 761, 706
Na-Alg powder	2911, 2322, 1592, 1397, 1020, 813, 704, 669
Acrylamide	3334, 3163, 2813, 1921, 1668, 1610, 1423, 1350, 1278, 1136, 1050, 839, 815, 666
AA+Am NCPC	3429, 3335, 3254, 2928, 1731,1673, 1615, 1595, 1456, 1151, 787, 716
WF NCPC	3429, 3331, 3253, 1673, 1592, 1456, 1148, 1082, 1031, 1002, 849,787, 715, 667, 614
Na-Alg NCPC	3429, 3334, 3254, 2321, 1697, 1683, 1594, 1457, 1149, 1062, 1002, 787, 715
After degradation	
AA+Am NCPC	3260, 3032, 2650, 2626, 2359, 1697, 1565, 1539, 1417, 1165, 939, 802
WF NCPC	3267, 3030, 2359, 1715, 1566, 1531, 1412, 1321, 1230, 922, 837, 774, 723
Na-Alg NCPC	2319, 1698, 1521, 1367,1017, 775

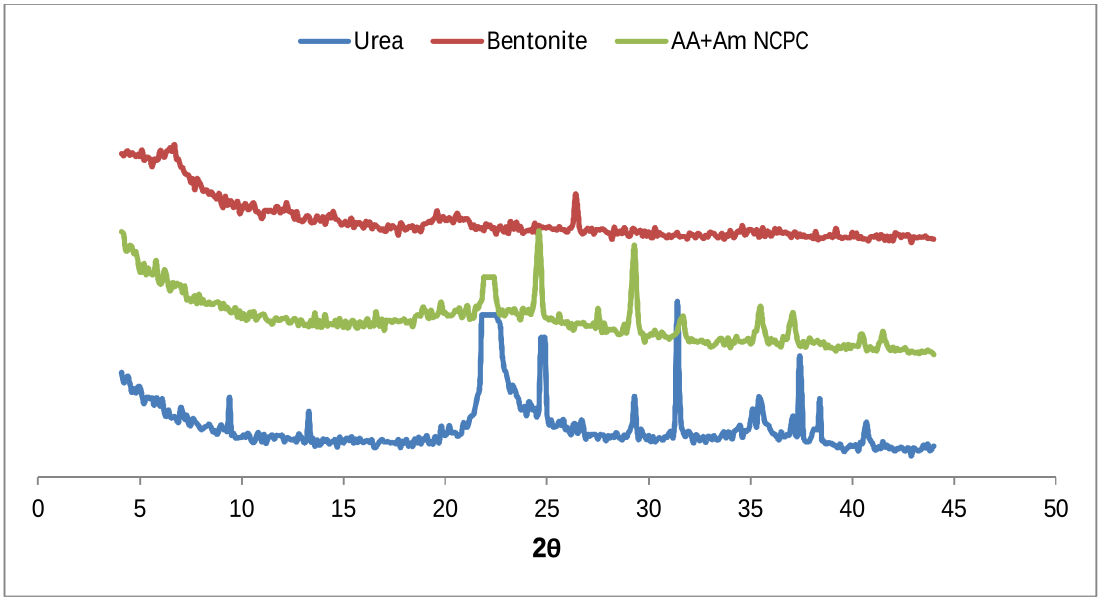


Figure 4.8 Random oriented powder XRD patterns of urea, bentonite and AA+Am NCPC

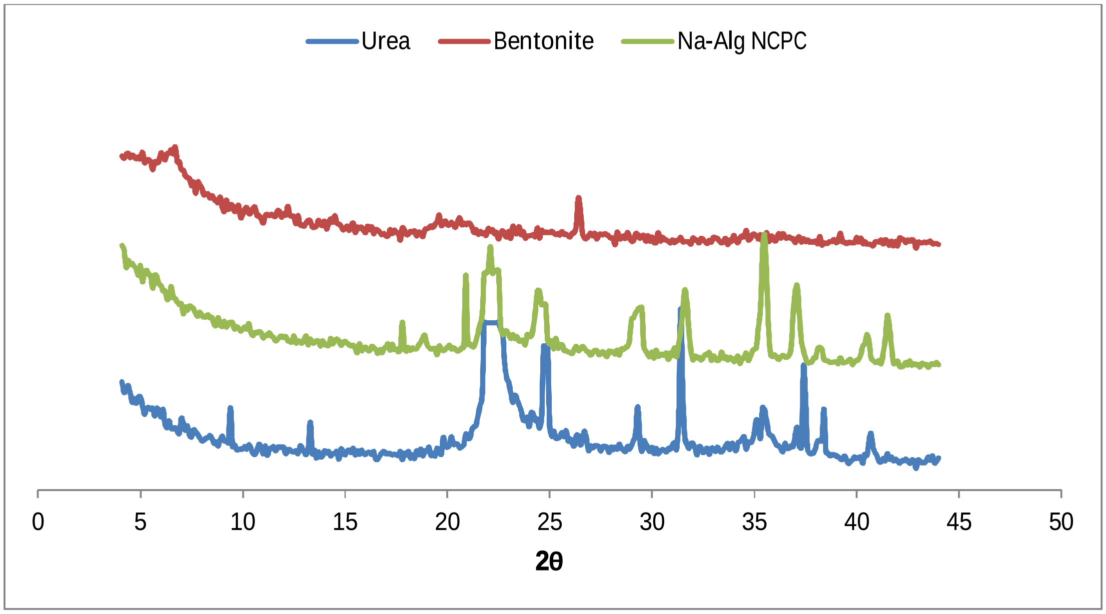


Figure 4.9 Random oriented powder XRD patterns of urea, bentonite and Na-Alg NCPC

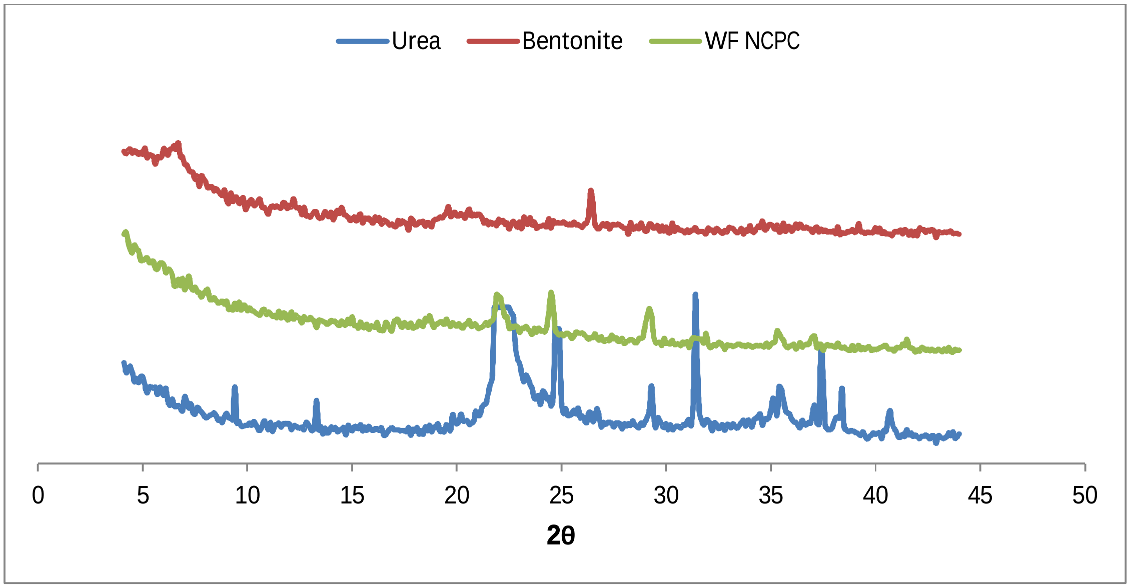


Figure 4.10 Random oriented powder XRD patterns of urea, bentonite and WF NCPC

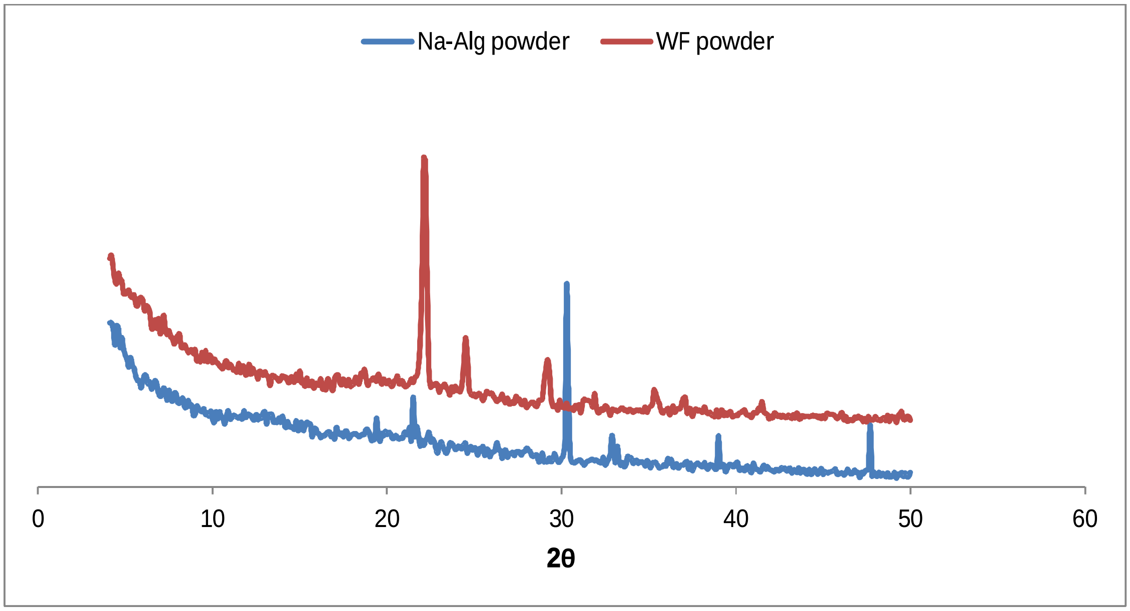
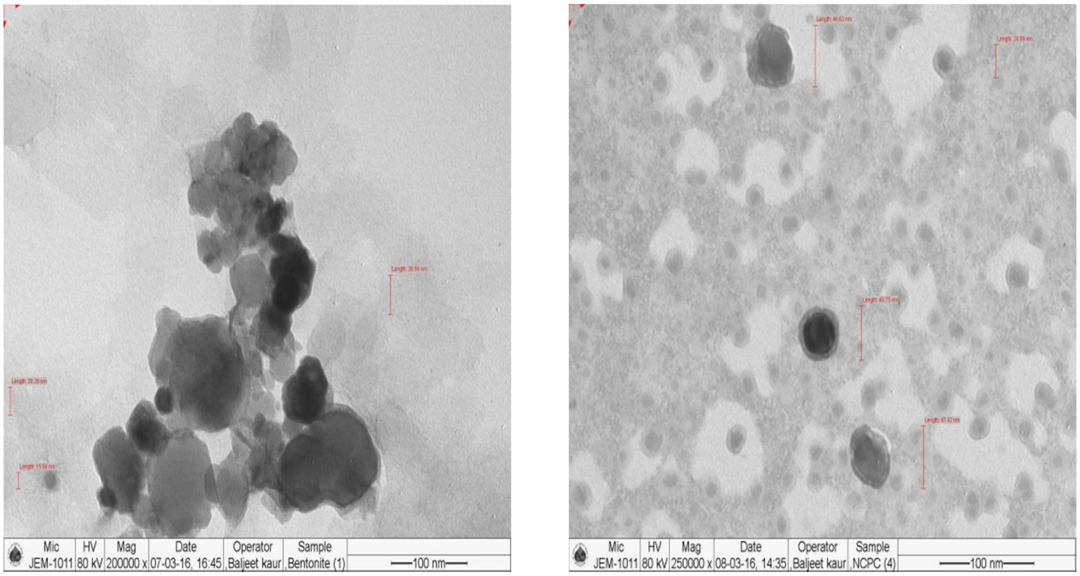
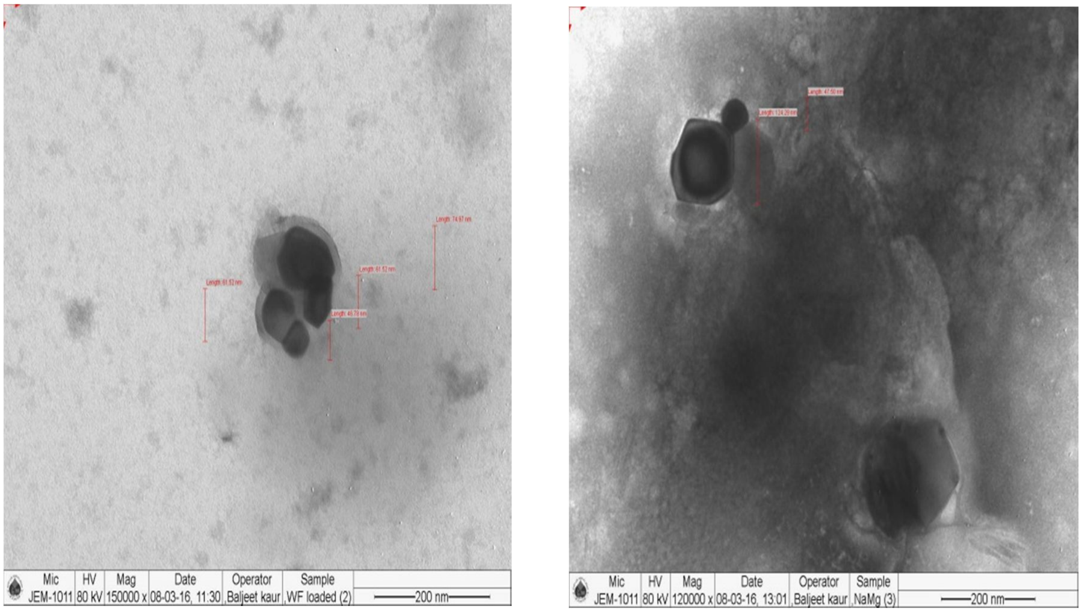


Figure 4.11 Random oriented powder XRD patterns of Na-Alg powder and WF powder

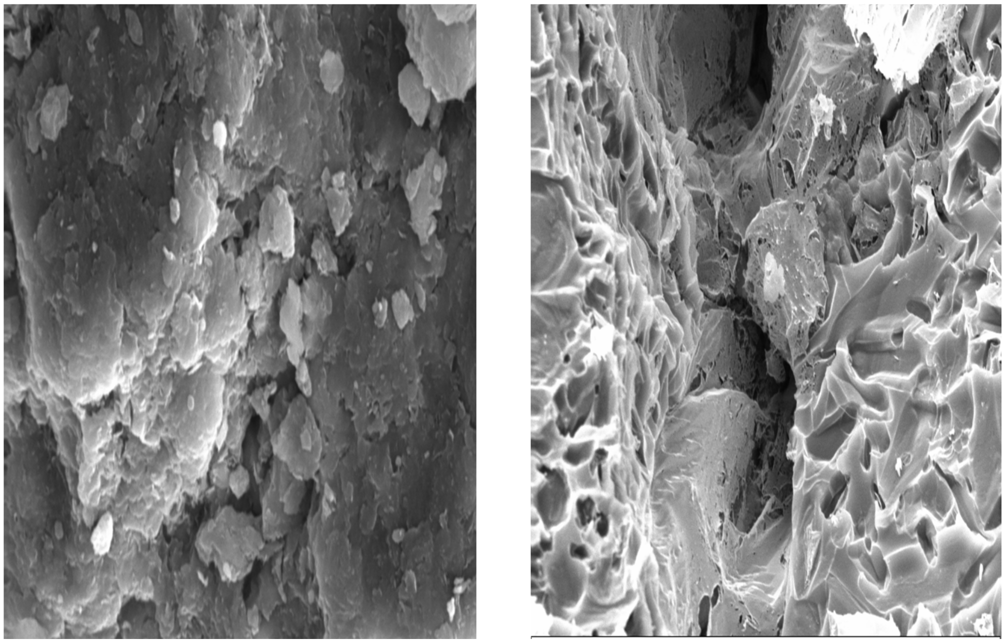


(a) Bentonite (b) AA+Am NCPC

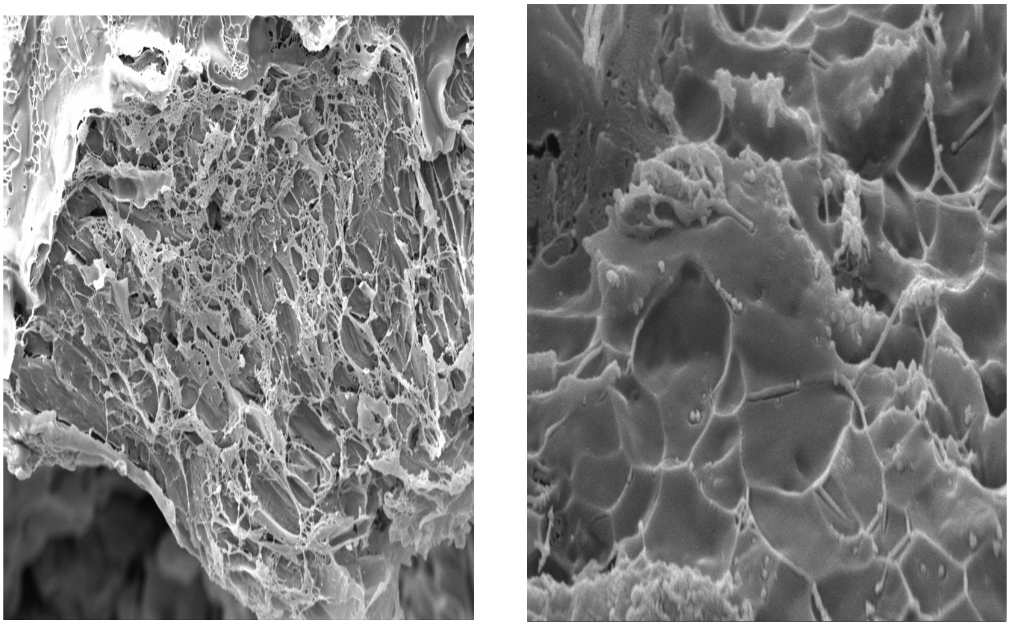


(c) WF NCPC (d) Na-Alg NCPC

Plate No. 4.1. Transmission electron microscopy (TEM) image of (a) bentonite, (b) AA+Am NCPC, (c) WF NCPC and (d) Na-Alg NCPC



(a) Bentonite (b) AA+Am NCPC



(c) WF NCPC (d) Na-Alg NCPC

Plate No. 4.2 Scanning electron microscopy (SEM) images of (a) bentonite, (b) AA+Am NCPC (c) WF NCPC and (d) Na-Alg NCPC

7, 14 and 30th day of incubation, respectively. Lower NO_3^- -N content was observed in all the treatment compared to urea. The NO_3^- -N content for AA+Am NCPC was 53.9, 77.8, 101.3 and 112.7 mg kg^{-1} soil, for WF NCPC 49.9, 80.2, 94.7 and 101.3 7 mg kg^{-1} soil, and for Na-Alg NCPC 43, 62.6, 83.7 and 99.47 mg kg^{-1} soil at 2, 7, 14 and 30th day of incubation, respectively (Figure 4.13b). Therefore, percentage of mineral N (NH_4+NO_3) out of total applied N (200 mg kg^{-1} soil) were found in this order: urea (87.22%) >AA+Am NCPC (63.77%) > WF NCPC (60%) > Na-Alg NCPC (59.91%) at 30th day of incubation (Figure 4.14).

4.2 Evidences of biodegradability

4.2.1 Degradation of NCPCs in soil

Effect of water levels on cumulative CO_2-C emission ispresented (Figure 4.17). Water level such as moistened condition hastened the CO_2-C evolution during decomposition of NCPCs. Higher cumulative carbon dioxide emission was observed in moistened condition than in flooding condition. Maximum cumulative carbon dioxide emission (0.725 and 0.602 mg d^{-1} g^{-1} soil) was found at 91 days after incubation in moistened and flooding conditions, respectively.

However, in treatments with moistened condition increased 16.28-18.80 % CO_2-C emission over flooding condition. Moistened condition enhanced the oxidation process of NCPC during incubation periods. Carbon emission was lower in anaerobic condition than in aerobic condition. The cumulative CO_2-C production significantly decreased with increasing moisture levels (moistened >flooding system) for the entire incubation period (Figure 4.17).

Cumulative CO_2-C evolution was increased with the increase in time both in moistened and flooded soil condition (Figure 4.15 and 4.16). Mixing of NCPCs with soil significantly increased cumulative CO_2-C. It brought roughly a 32% increase in cumulative CO_2-C production in WF NCPC treated soil compared to control followed by Na-Alg NCPC treated soil (28.23%) and AA+Am NCPC (14.19%) in moist condition. In flooded condition the increase in the cumulative CO_2-C production compared to control followed the similar trend: WF NCPC (29.79%) > Na-Alg NCPC (22.53%) >AA+Am NCPC (10.07%). The lowest cumulative CO_2-C evolution was found in 3 days after incubation (0.065 mg in control, 0.106 mg in AA+Am NCPC, 0.111 mg in Na-Alg NCPC and 0.108 mg in WF NCPC), and the maximum CO_2-C evolution (0.611 mg in control, 0.698 mg in AA+Am NCPC, 0.784

mg in Na-Alg NCPC and 0.805 mg in WF NCPC) was obtained from 91 days after incubation in moistened soil condition(Figure 4.15). Whereas, for flooded condition the lowest cumulative CO_2-C evolution was found in 3 days after incubation (0.057 mg in control, 0.093 mg in AA+Am NCPC, 0.098 mg in Na-Alg NCPC and 0.099 mg in WF NCPC), and the maximum CO_2-C evolution (0.520 mg in control, 0.548 mg in AA+Am NCPC, 0.607 mg in Na-Alg NCPC and 0.644 mg in WF NCPC) was obtained (Figure 4.16).

4.2.2 Weight loss

Figure 4.18 presents the percentage weight loss of nanocomposites during 90 days of soil burial. At the initial stage, the weight loss increased rapidly as a function of exposure time. The process of biodegradation of NCPCs was found to be continuous and the percentage weight loss was found to increase with increasing number of days. The rapid biodegradation rate was found in all the NCPCs up to 60 days of burial time. From Figure 4.18, it can be seen that the weight loss of the AA+Am NCPC is lower as compared to the WF and Na-Alg NCPC. WF NCPC was found to be degrading up to 32.8%, whereas Na-Alg and AA+Am NCPC were found to be degrading up to 23.12% and 11.2% respectively.

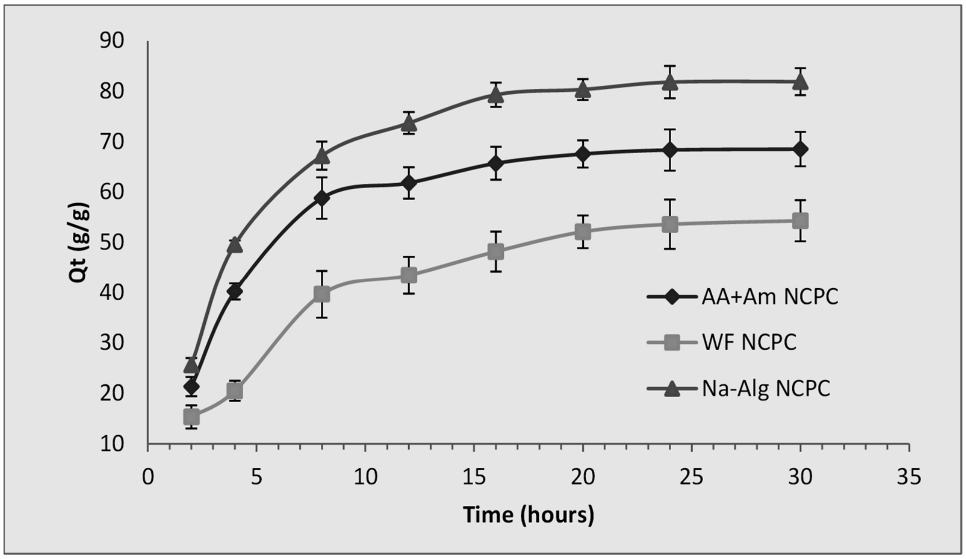
4.2.3 FTIR Spectra

FTIR spectra of AA+Am, WF and Na-Alg NCPC before and after degradation were shown in Figure 4.19, 4.20 and 4.21. Degraded samples of WF NCPC showed variation in the peaks as compare to the FTIR peaks obtained in the spectrum of crosslinked polymer before degradation. The spectrum of WF NCPC exhibited most of the characteristic adsorption peaks of native WF NCPC but with some differences (Figure 4.20). The bands between 3000- 3429 cm^{-1} for O–H stretching disappeared. The peak at 1002 cm^{-1} is due to stretching vibrations of C–O from glycosidic bond in WF NCPC which was disappeared after degradation. The intensity of peaks initially observed at 3253, 1592, 1148, 849, 787 and 723 cm^{-1} was found shifted after degradation. Thus, FTIR spectra confirmed that the grafted chains of NCPCs got biodegraded.

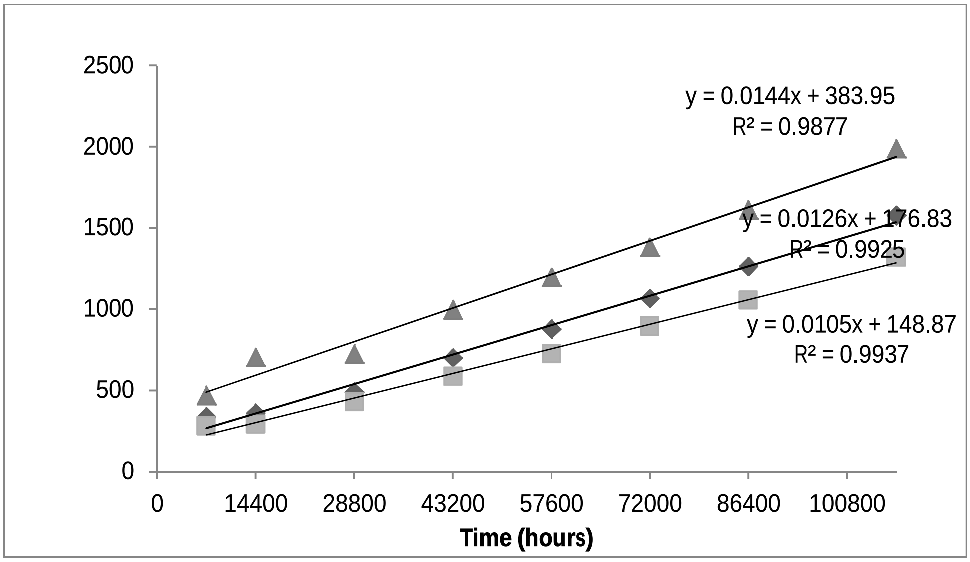
FTIR spectra of AA+Am NCPC before and after degradation were recorded (Figure4.21). The FTIR of AA+Am NCPC showed peaks at 2928 cm^{-1} (─OH stretching of AA), 1731 cm^{-1}(C=O stretching of amide band), 1456 cm^{-1} (NH in

Table 4.3 Weight % of various elements in NCPCs obtained from SEM-EDX

	C	**N**	**O**	**Al**	**Si**	**Fe**	**Na**	**Total**
Bentonite	50.42	-	47.42	0.81	1.35	-	-	100
WF NCPC	45.18	19.63	34.52	-	0.66	-	-	100
AA+AM NCPC	46.63	22.16	28.12	0.66	1.33	1.10	-	100
Na-Alg NCPC	43.06	25.73	28.79	0.47	0.85	-	1.10	100

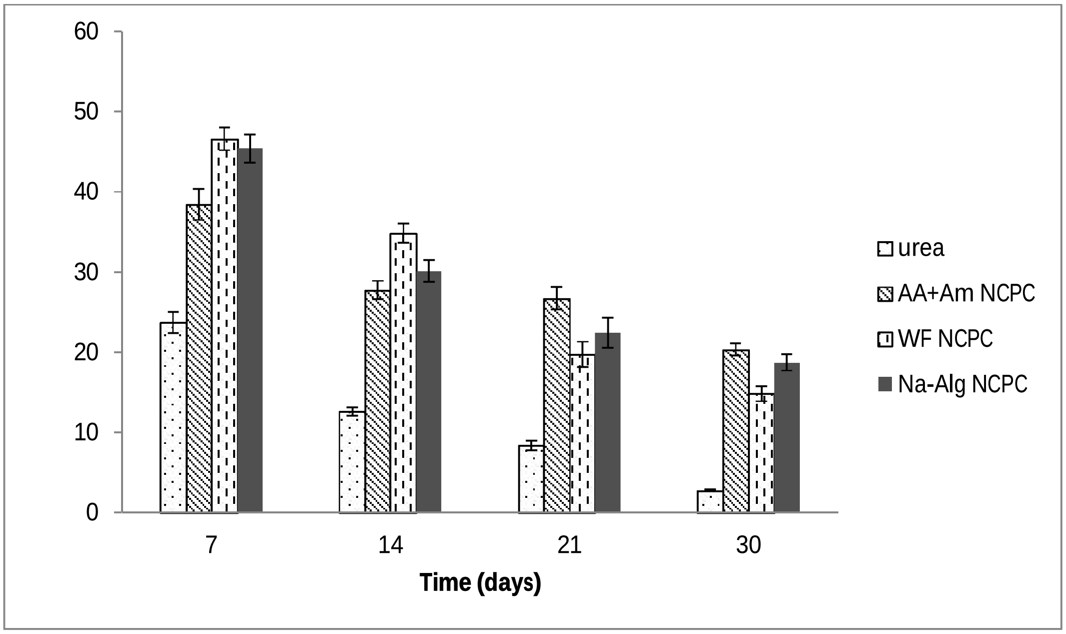


(a)

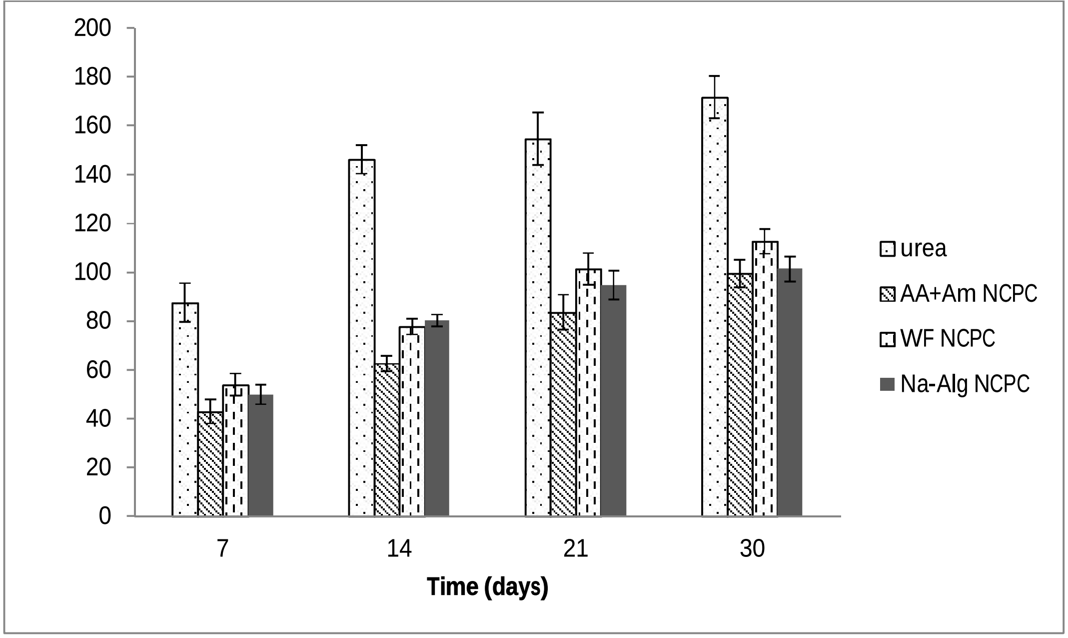


(b)

Figure.4.12. Swelling kinetic curves of NCPCs in distilled water (a) and t/Q_t versus t (b) graphs of NCPCs



(a)



(b)

Fig.4.13. Release behavior of (a) NH_4^+ mg kg^{-1} soil and (b) NO_3^- mg kg $^{-1}$ soil from NCPCs in soil

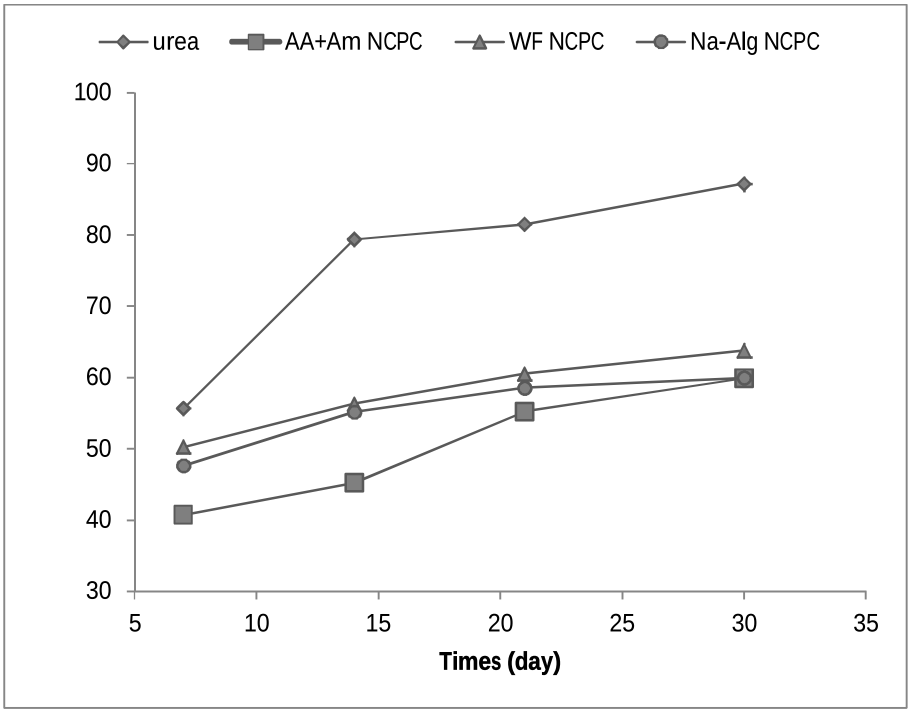


Figure.4.14. Nitrogen release behavior from different NCPCs in soil

plane bending of amide band) and 1151 cm^{-1} (CN stretching vibrations of amide. Degraded samples of AA+Am NCPC showed variation in the peaks as compare to the FTIR peaks obtained in the spectrum of crosslinked polymer before degradation. The intensity of the peaks initially observed at 1731, 2928, 1456 cm^{-1} and 1166.0 $cm^{-1}$was found shifted after biodegradation.

The peak at 1002 cm^{-1} is due to stretching vibrations of C–O from glycosidic bond in Na-Alg NCPC which was disappeared after degradation (Figure 4.19). The spectrum of biodegraded NaAlg NCPC exhibited very few of the characteristic adsorption peaks of native alginate NCPC. For instance, the bands between 3000-3429 cm^{-1} for O–H stretching, the band at 1683 cm^{-1} related to the stretching vibration of the carbonyl groups of AA disappeared, at 1594 and 1457–1410 cm^{-1} were assigned to the asymmetric and symmetric stretching vibration of the $–COO^{-}$ groups, respectively, at 1062 cm^{-1} and 1037 cm^{-1} for C–O stretching were completely shifted or disappeared.

4.3 Growth parameters

The plant height observed in control T_1 (65 cm) for rice was shorter, as compared to the fertilized plants at the harvesting time (Table 4.4). In rice 90.6 cm was the greatest height of plants when treated with T_2, followed by T_5 (88.14 cm), T_7 (86.4 cm) and T_9 (85.13cm) performed well. The range of panicle length varied from 16 cm (T_1) to 26.45 cm (T_2). The insignificant differences were observed in treatments T_2, T_5, T_7 and T_9.

Data pertaining to plant height of wheat crop (Table 4.4) revealed that addition of fertilizer treatments significantly ($P < 0.05$) increased the plant height over control (50.60 cm). Plant height recorded under T_2 (71.43 cm) was highest and remained statistically different with other treatments. Data regarding effect of different treatments on spike length (cm) of wheat is summarized in (Table 4.4). Spike length was found significantly highest under the treatments T_2 (9.60 cm), which remained at par with T_7 (9.45 cm), T_9 (9.34 cm), T_5 (9.17 cm), T_6 (8.83 cm) and T_{10} (8.78 cm). The spike length increased while increasing N rate from 60 to 90 kg N ha^{-1} and when different sources are applied at 75% N dose: Urea (8.4 cm), WF NCPC (9.17 cm), Na-Alg NCPC (9.45 cm) and AA+Am NCPC (9.34 cm).

4.3.1 Yield components

4.3.1.1 Straw and grain yield

Fertilizer treatments significantly increased the straw yield in fertilized pots as compared to control in case of rice crop (Table 4.5). Maximum straw yield was found in the treatment T_2 (15.52 g/pot) followed by T_5 (15.50 g/pot), T_9 (15.22 g/pot), T_7 (15.13 g/pot), T_3 (14.07 g/pot) and T_{10} (13.54 g/pot). Treatments T_5, T_7 and T_9 showed 34, 36 and 37% increment in grain yield compared to control (Figure 4.23a). Different fertilizer application significantly increased the rice grain yield as compared to control. Maximum grain yield of 8.35 g/pot was recorded under treatment T_2 which remained statistically insignificant with the treatment T_5 (8.06 g/pot), T_6 (7.69 g/pot), T_7 (8.21 g/pot), T_8 (7.62 g/pot), T_9 (8.27 g/pot) and T_{10} (7.77 g/pot). Treatments applied at 75% and 50% N of RDF through NCPCs showed insignificant difference in grain yield with conventional fertilizer at 100% N of RDF.

Application of fertilizer treatments in wheat crop significantly increased the straw yield as compared to control. Maximum straw yield of 11.80 g/pot were obtained with the application treatment T_2 (Table 4.5) and did not vary significantly with the treatments T_5 (10.98 g/pot). Application of fertilizer treatments in wheat crop significantly increased the grain yield over control. Treatments T_5, T_7 and T_9 showed 59, 57 and 60% increment in grain yield compared to control (Figure 4.23b). The lowest grain yield of 4.80 g/pot was recorded under T_1 (control) and the highest grain yield of 7.69 g/pot in wheat was recorded under T_9 accounted an increase of 60.2 per cent over control, followed by the grain yield of 7.65 g/pot (T_5), 7.53 g/pot (T_7), were statistically ($P<0.05$) insignificant with T_2 (7.61 g/pot). Treatments containing 50% N of RDF in NCPCs (T_6, T_8 and T_{10}) produced significantly higher grain yield of 6.63, 7 and 7.00 g/pot, respectively compared to conventional fertilizer at 50 and 75% dose and even performed equally with 100% RDF treatment (T_2). The relationship between panicle /spike length and grain yield was strongly correlated ($R^2 = 0.812$ for rice and $R^2 = 0.863$ for wheat) and statistically significant as shown in the Figure 4.22.

4.3.2 Straw and grain N%

Data pertaining to concentration of N in rice straw presented in Table 4.6 the data revealed that crop grown under different fertilizer treatments significantly increased straw N concentration over control (T_1). The concentration of N in straw ranged from

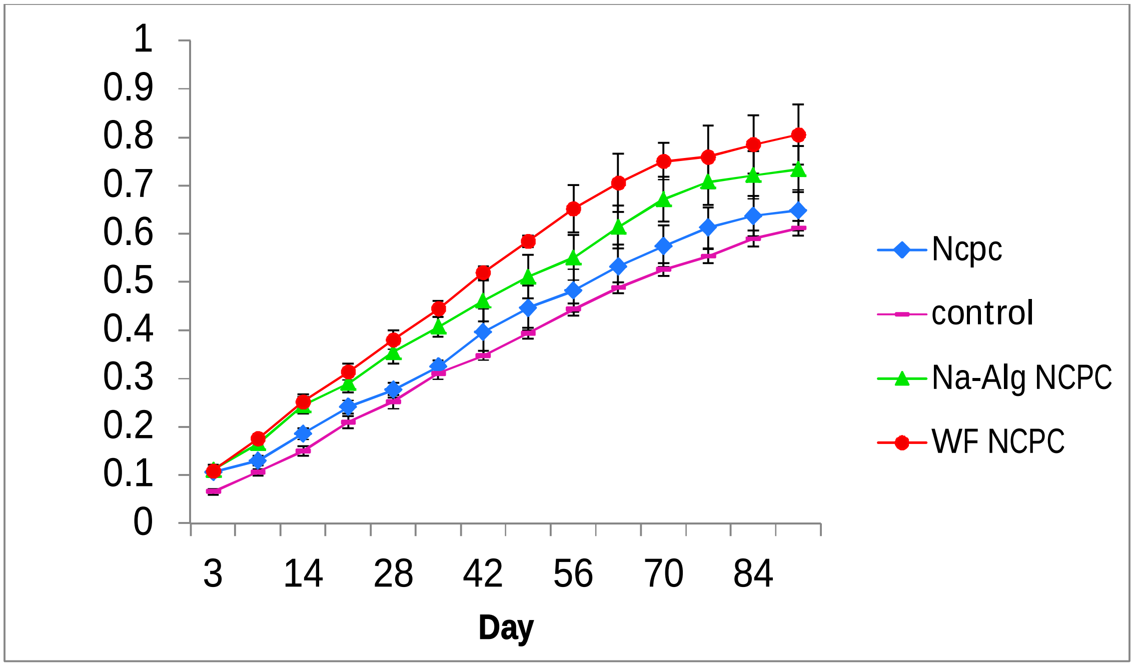


Figure.4.15 Effect of different fertilizer treatments on cumulative CO_2-C (mg/g) evolution in moist soil condition

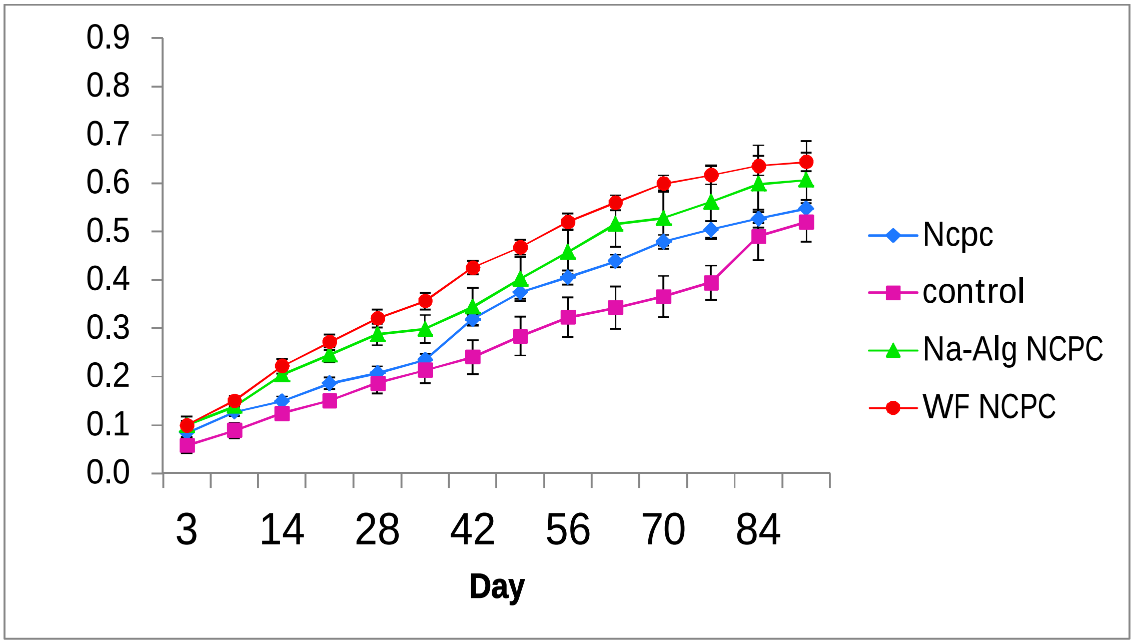


Figure.4.16 Effect of different fertilizer treatments on cumulative CO_2-C (mg/g) evolution in flooded soil condition

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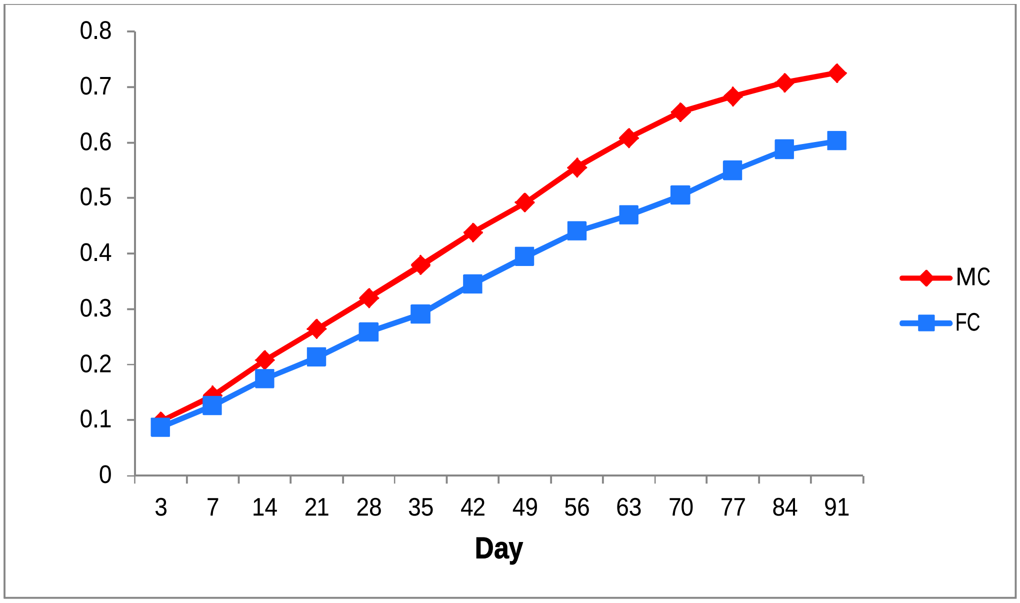


Figure.4.17 Cumulative CO_2-C evolution at different water levels

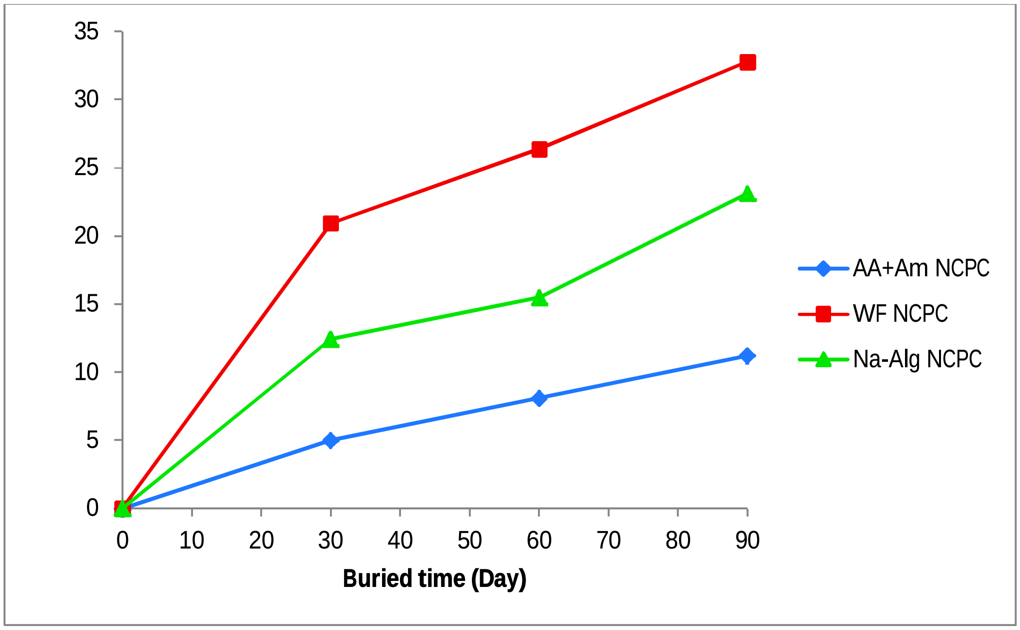


Figure 4.18 Degradation behavior of different NCPCs versus incubation time after degradation for 90 days.

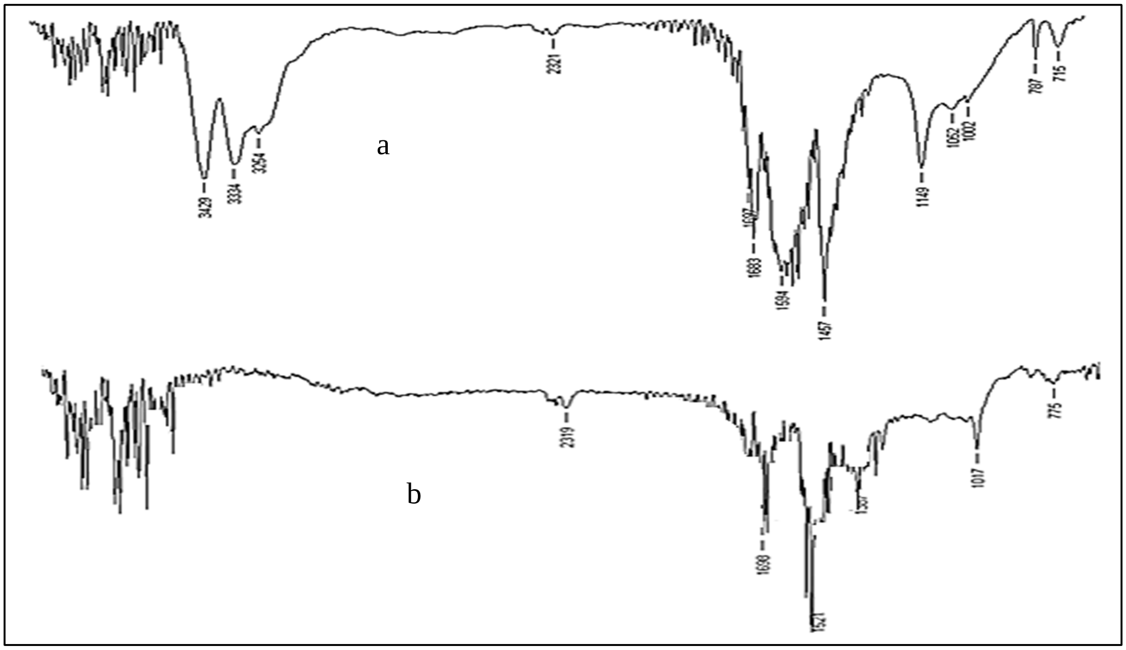


Figure 4.19 FTIR spectra of Na-Alg NCPC before (a) and after (b) degradation

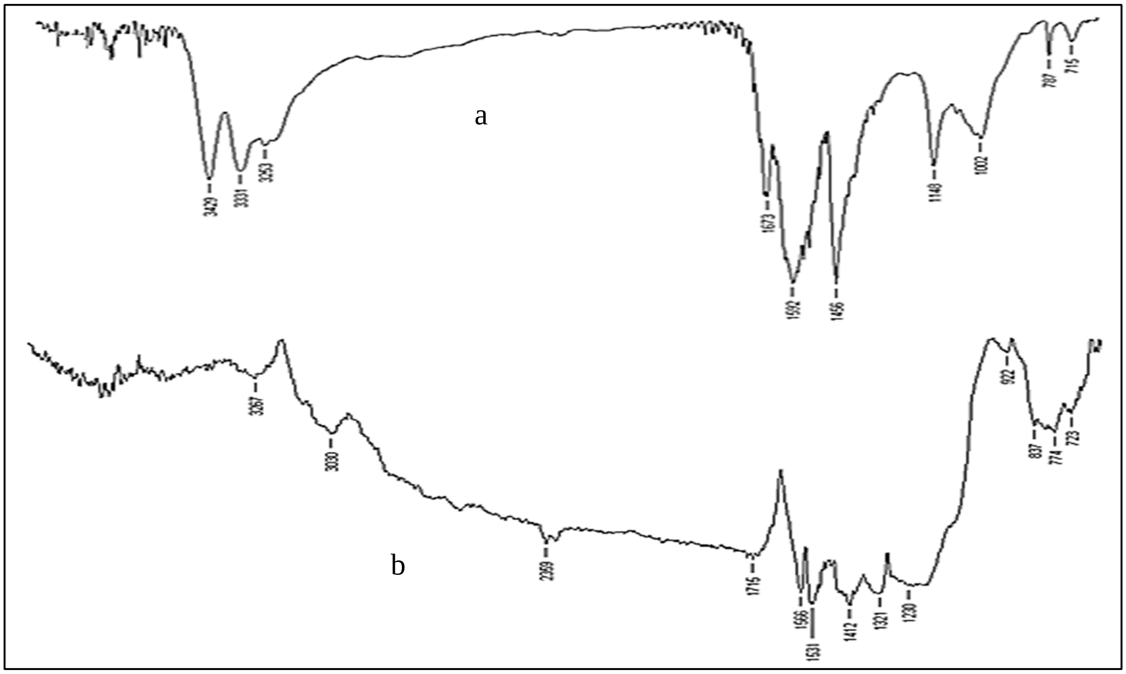


Figure 4.20 FTIR spectra of WF NCPC before (a) and after (b) degradation

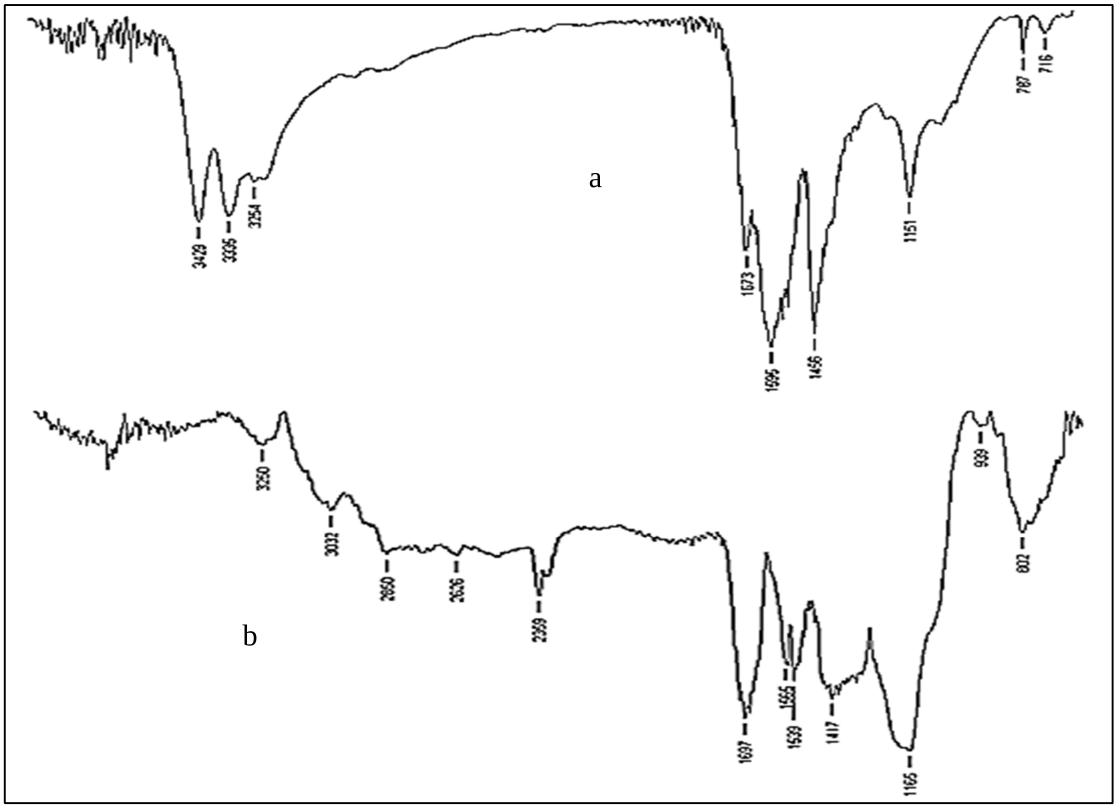


Figure 4.21 FTIR spectra of AA+Am NCPC before (a) and after (b) degradation

0.45% (T_1) to 0.56% under T_5 and T_7. Higher concentration of N was found under the T_5 (0.56%), T_7 (0.56%) and T_9 (0.55%) respectively, which remained statistically insignificant. Treatment T_5 and T_7 showed 24.4% of increment on N in straw as compared to control (T_1). Grain N concentration in rice (Table 4.6) increased significantly ($p < 0.05$) with application of fertilizers over control (T_1). Highest N concentration (1.34%) was found under T_7 and which remained insignificantly different with the other N applied treatments.

Lower nitrogen concentration in wheat straw was observed in treatments where nitrogen fertilizer was applied as urea at 100, 75 and 50% of RDF (Table 4.6). The concentration of N in wheat straw ranged from 0.39% in control (T_1) to 0.53% (T_7 and T_9). Straw nitrogen concentration was found maximum in treatments T_9 and T_7 which was equal in value i.e. 0.53%, followed by T_{10} (0.52%) and T_5 and T_8 (0.50%). The range of nitrogen in wheat grain varied from 1.76 % in control (T_1) to 2.11% (T_2 and T_7). All other treatments showed statistically significant difference only with 50% RDF treatment (T_4) for N concentration in grain.

4.3.3 Nitrogen uptake by straw and grains

Nitrogen uptake by rice straw (Table 4.7) increased significantly ($p < 0.05$) with application of both conventional as well as NCPC fertilizers than control (48.47 mg/pot). Nitrogen uptake by rice straw (86.80 mg/pot) recorded under T_5 was highest but remained significantly at par with T_7 (84.73mg/pot), T_2 (83.81 mg/pot), and T_9 (83.71 mg/pot). Grain N uptake by rice (Table 4.7) increased significantly ($p < 0.05$) with the application of fertilizer treatments as compared to control (T_1). N uptake by rice grain (110.22 mg/pot) under T_2, (110.01 mg/pot) under T_7, T_9 (109.99 mg/pot) and (107.20 mg/pot) under T_5 was significantly higher than any other treatments and gave 80.95, 80.64, 80.60 and 76.02 % higher N uptake as compared to control (T_1).

Differences in nitrogen uptake by straw and grains of wheat due to application of different treatments are presented in Table 4.7. It is evident from the data that application of fertilizers significantly increased the N uptake in straw and grains of wheat as compared to control. In both plant parts maximum N uptake was recorded in the pots treated with T_9 (217.99 mg/pot) and remained statistically insignificant with T_2, T_5 and T_7. The lowest straw N uptake of 32.64 mg/pot was recorded under T_1 (control) and highest straw N uptake of 56.50 mg/pot was recorded in treatment T_9 which accounted for an increase of 73.10 per cent over control (T_1). Application of NCPC fertilizers (75% N of RDF) T_9, T_7 and T_5 significantly increased the grain N uptake of 161.49, 158.88 and 154.53 mg/pot, respectively, remained insignificantly different with T_2 (160.57 mg/pot).The relationship between nitrogen uptake and grain yield was strongly correlated (R^2 = 0.976 for rice and R^2 = 0.947 for wheat) and statistically significant as shown in the Figure 4.24.

4.3.4 Nitrogen use efficiency

Application of NCPCs at 75% and 50% N of RDF significantly improved recovery efficiency (ARE), agronomic efficiency (AE) and physiological efficiency (PE) as compared to control and conventional fertilizer application at different doses in rice crop (Table 4.8). The lowest recovery efficiency (39.75%), agronomic efficiency (10.89 g/g N) recorded in T_2 i.e. with 100% conventional fertilizer dose and lowest physiological efficiency 23.99 g/g N observed in T_5. ARE was found higher in treatment T_{10} (56.54 %) and remained statistically insignificant with other NCPCs treatment at both levels. Maximum AE was found in T_{10} (16.26 g/g N) followed by T_6 (15.51 g/g N) and maximum PE was recorded in the treatment T_6 (29.21 g/g N) followed by T_{10} (28.76 g/g N).

Similar trend was observed in case of recovery efficiency, agronomic efficiency and physiological efficiency by wheat (Table 4.8). Recovery efficiency had maximum values in the treatment T_{10} (68.52 %) followed by T_8 (66.75 %). Similar trend was observed in agronomic efficiency, where lowest efficiency was observed in case of T_2 (13.19 g/g N) and highest in T_8 and T_{10} (20.56 g/g N) followed by T_9 (18.06 g/g N). The PE was found highest in NCPC treatment T_6 (30.88 g/g N) followed by T_8 (30.80 g/g N).

4.3.5 Micronutrient content in grain

Application of different nitrogen fertilizer treatments significantly increased uptake of micronutrient in rice grains (Table 4.9). Higher content of Fe, Zn, Cu and Mn was found in T_7 (27.03, 30.8, 2.04 and 31.18 mg kg^{-1} respectively) which remained statistically at par with T_9 (27.5, 30.3, 1.98 and 31.7 mg kg^{-1} respectively). Concentration of Fe and Zn in treatments receiving 75% N of RDF through NCPCs (T_5, T_7 and T_9) were significantly higher or at par with the treatment T_2 (100% N of RDF through urea).

Table 4.4 Effect of different treatments on the growth contributing characters of rice and wheat

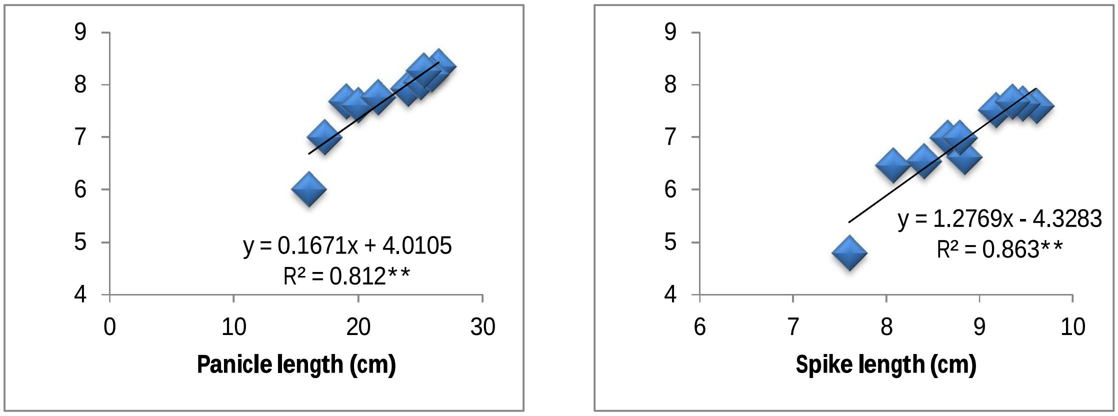
Treatment	**Rice**		**Wheat**	
	Plant height (cm)	**Panicle length (cm)**	**Plant height (cm)**	**spike length (cm)**
T1	65.00 ^{f}	16.00 ^{f}	50.60 ^{e}	7.60 ^{e}
T2	90.60 ^{a}	26.45 ^{a}	71.43 ^{a}	9.60 ^{a}
T3	78.90 ^{bcd}	24.00 ^{b}	64.87 ^{b}	8.40 ^{cde}
T4	68.80 ^{ef}	17.30 ^{e}	57.9 ^{cd}	8.07 ^{de}
T5	88.14 ^{a}	25.00 ^{ab}	64.23 ^{bc}	9.17 ^{abc}
T6	77.56 ^{cd}	19.00 ^{de}	58.8b ^{cd}	8.83 ^{abcd}
T7	86.40 ^{ab}	25.89 ^{ab}	62.17 ^{bcd}	9.45 ^{ab}
T8	74.23 ^{de}	20.00 ^{cd}	57.21 ^{d}	8.65 ^{bcd}
T9	85.13 ^{abc}	25.28 ^{ab}	63.67 ^{bc}	9.34 ^{ab}
T10	72.50 ^{def}	21.56 ^{c}	58.2 ^{cd}	8.78 ^{abcd}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

Table 4.5 Effect of different treatments on the yield contributing characters of rice and wheat

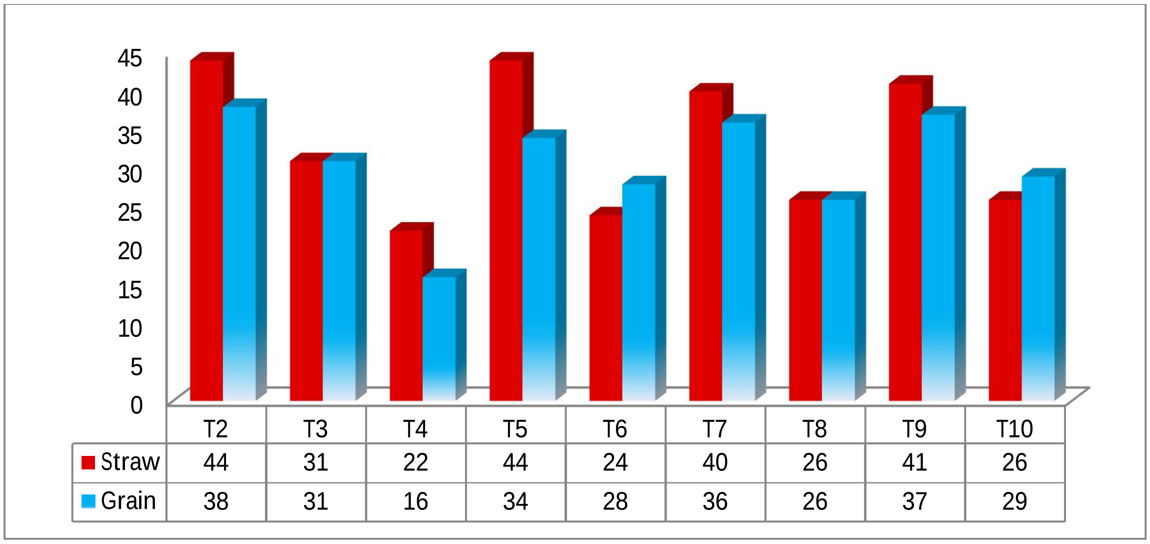
Treatment	Rice		Wheat	
	Straw yield (g/pot)	**Grain yield (g/pot)**	**Straw yield (g/pot)**	**Grain yield (g/pot)**
T1	10.77^{e}	6.03^{c}	8.37^{d}	4.80^{c}
T2	15.52^{a}	8.35^{a}	11.80^{a}	7.61^{a}
T3	14.07^{bcd}	7.93^{b}	10.66^{bc}	6.55^{b}
T4	13.10^{d}	7.01^{bc}	9.82^{c}	6.48^{b}
T5	15.50^{ab}	8.06^{ab}	10.98^{ab}	7.65^{a}
T6	13.40^{d}	7.69^{ab}	9.60^{c}	6.63^{ab}
T7	15.13^{abc}	8.21^{ab}	10.21^{bc}	7.53^{a}
T8	13.57^{cd}	7.62^{ab}	9.85^{c}	7.00^{ab}
T9	15.22^{ab}	8.27^{a}	10.66^{bc}	7.69^{a}
T10	13.54^{d}	7.77^{ab}	9.97^{bc}	7.00^{ab}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan's Multiple Range Test (DMRT).

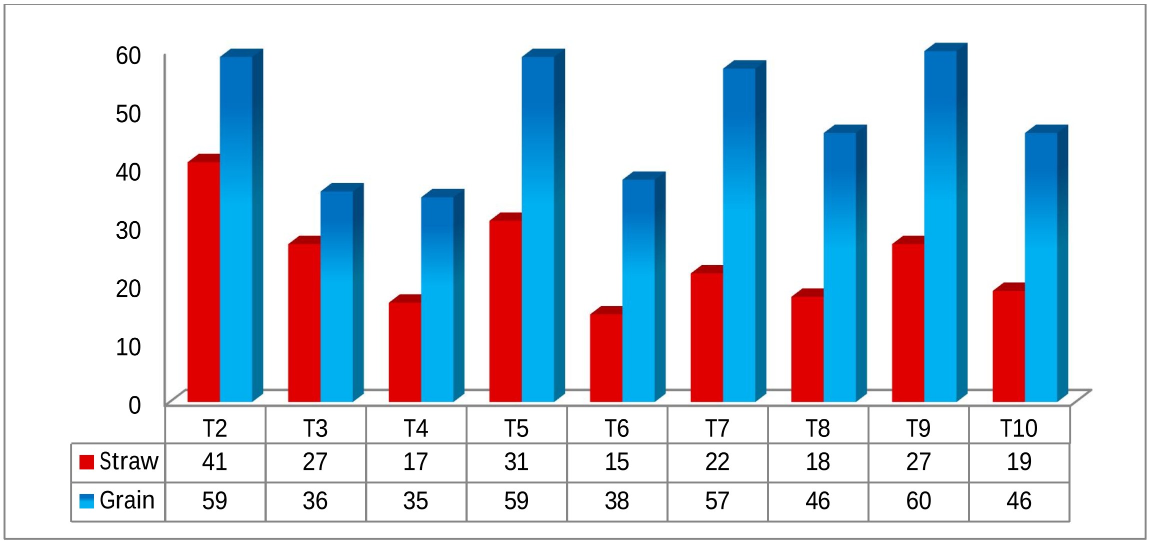


(a) (b)

Figure.4.22 Relationship between (a) grain yield and panicle length of rice and (b) grain yield and spike length of wheat



(a)



(b)

Figure 4.23 Effect of different treatments on percent yield increase over control of (a) rice and (b) wheat

Uptake of micronutrient (Fe, Zn, Cu and Mn) in grain was significantly influenced by the different treatments. Micronutrient in wheat grain is presented in Table 4.9. Highest uptake of Fe, Zn, Cu and Mn was found in T_7 (43.6, 41.9, 6.88 and 41 mg kg^{-1}, respectively) and remained statistically at par with treatments T_9 (42.20, 41.60, 7.02 and 41.1 mg kg^{-1}, respectively) and T_5 (41.40, 40.4, 6.25 and 39.34 mg kg^{-1}, respectively). Similarly lowest uptake of these elements was recorded in treatment T_1 (37, 35.2, 4.82 and 36.07 mg kg^{-1}, respectively).

4.3.6 Chlorophyll concentrations in leaves

Considering the effect of different fertilizer treatments significantly influenced the chlorophyll concentration in rice leaves (Table 4.10). Maximum concentration of chlorophyll a was observed in T_2 (1.50 mg/g), whereas, maximum concentration of chlorophyll b was found in T_7 (1.24 mg/g) followed by T_9 and T_5 (1.02 mg/g).

The chlorophyll concentrations (chlorophyll a, chlorophyll b and total chlorophyll) in wheat leaves were estimated to predict plant's health and photosynthetic capacity in response to different fertilizer treatments. Chlorophyll content was found higher in fertilizer treated plants as compared to control (Table 4.10). T_2 resulted in highest (2.25 mg/g) total chlorophyll content and T_4 resulted in lowest (0.90 mg/g) total chlorophyll content among the fertilized treatments. The concentration of total chlorophyll in leaves resulting from the different treatments generally declined in the order T_2 (2.25 mg/g) > T_7 = T_9 (1.97 mg/g) > T_5 (1.90 mg/g) > T_3 (1.73 mg/g) > T_8 (1.66 mg/g) > T_{10} (1.55 mg/g) > T_6 (1.52 mg/g) > T_4 (0.90 mg/g) > T_1 (0.75 mg/g). The relationship between chlorophyll content and straw N uptakewas strongly correlated ($R^2 = 0.853$ for rice and $R^2 = 0.852$ for wheat) and statistically significant as shown in the Figure 4.25.

4.3.7 Soil NH_4, NO_3 and mineral N content under rice

4.3.7.1 NH_4^+-N

Application of different fertilizer treatments significantly influenced ammonium N in soil during the crop growth periods. The NH_4^+-N content of soil under rice was higher in soil fertilized with urea and other NCPCs compared to that of the no-N control treatment (Table 4.11). In general the NH_4^+-N content in soil decreased with the advancement of crop growth and become lowest at the time of harvest. The NH_4^+-N content in soil showed three peaks, which appeared after urea applications. At 3 DAT, the mean value of NH_4^+-N content in soil ranged from 12.79 mg kg^{-1} in T_1 to 27.94 mg kg^{-1} soil in T_2 (Table 4.11). While, at harvest of the crop (105 DAT), the mean value of NH_4^+-N in soil ranged from 1.03 in T_1 to 2.42 mg kg^{-1} in T_5. Significantly higher amount of NH_4^+ -N content was observed in T_2 after fertilizer application because of quick urea hydrolysis. There is a sharp increase of soil N concentration after fertilizer application and a significant decline during the period of maximum N crop absorption. Among the three NCPCs, WF NCPC (@ 75 % RDF) maintained highest soil ammonium just after the fertilization because of quick release of ammonium through hydrolysis. Whereas, AA+Am NCPC and Na-Alg NCPC (@ 75 % RDF) maintained less amount of NH_4^+ -N in soil initially but on later stage they maintained significantly higher NH_4^+ -N in soil compared to T_2 due to slow release of the ammonium. Soil receiving the treatment T_9 most effectively controlled the NH_4^+ -N release in soil on most of the sampling date indicating that this fertilizer was able to release NH_4^+ -N slowly in soil and maximum absorption by the crops leading to less loss of N. Contents of soil NH_4^+ -N for all NCPCs were evidently lower than conventional fertilizer T_2, which trended to decrease more slowly throughout the growing periods. After the fertilizer application in both T_7 and T_9, the NH_4^+ -N content was higher at the end (2.38 mg kg^{-1} for T_7 and 2.42 mg kg^{-1} for T_9 on 105 DAT). It was also observed that lower level of fertilizers (@ 50%) as T_6, T_8 and T_{10} were more effective in maintaining availability of NH_4^+-N content in soil as compared to fertilizer in conventional form (T_4).

4.3.7.2 NO_3^- content

Among the fertilized treatments, the NO_3^--N content was highest in T_2 throughout the study period due to quick release of ammonium and its subsequent nitrification. Unlike the NH_4^+-N content in rice, the level of NO_3-N in soil was lower in the T_7 and T_9 as compared to T_2 across the entire crop growing period except on 20 DAT. After T_2 the NO_3^--N content under T_3 and T_5 was maximum due to fast release of N from it. Soil nitrate content increased after split applications of urea and NCPCs. The NO_3^- -N content under urea applied treatments were significantly higher over control (T_1) throughout the growing period (Table 4.12). At later stages of crop growth the content of NO_3^--N in soil at lower level of conventional fertilizer (T_4) application exhausted and remained at par with control. At 3 DAT, the mean value of NO_3^--N content in soil ranged from 7.80 mg kg^{-1} in T1 to 12.73 mg kg^{-1} soil in T_2 (Table

Table 4.6 Effect of different treatments on Nitrogen content of grain and straw in rice and wheat

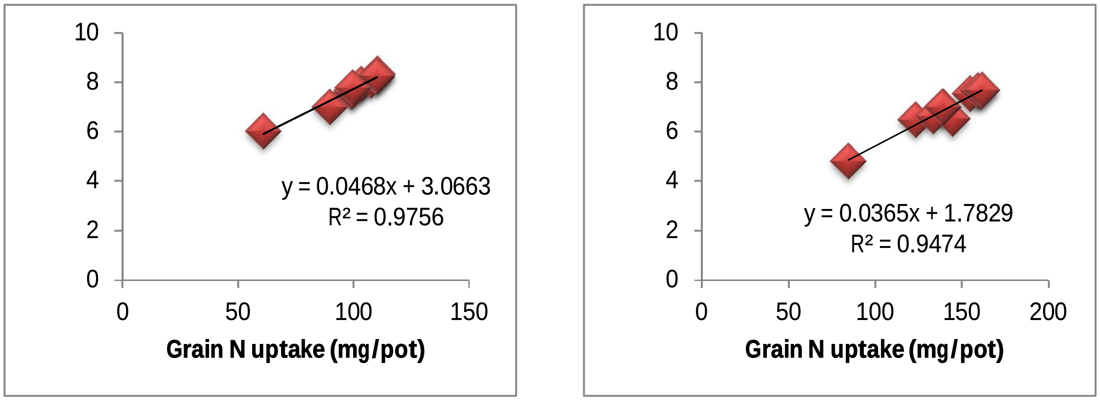
Treatment	**Rice**			**Wheat**		
	Straw N%	**Grain N%**	**Total N%**	**Straw N%**	**Grain N%**	**Total N%**
T1	0.45^{c}	1.01^{b}	1.46^{c}	0.39^{e}	1.76^{c}	2.15^{c}
T2	0.54^{ab}	1.32^{a}	1.86^{a}	0.47^{cd}	2.11^{a}	2.58^{a}
T3	0.53^{ab}	1.3^{a}	1.83^{a}	0.46^{cd}	2.07^{a}	2.53^{a}
T4	0.48^{c}	1.28^{a}	1.76^{b}	0.44^{d}	1.90^{b}	2.34^{b}
T5	0.56^{a}	1.33^{a}	1.89^{a}	0.50^{abc}	2.02^{a}	2.52^{a}
T6	0.5^{b}	1.29^{a}	1.79^{a}	0.48^{bcd}	2.01^{a}	2.49^{a}
T7	0.56^{a}	1.34^{a}	1.90^{a}	0.53^{a}	2.11^{a}	2.64^{a}
T8	0.52^{ab}	1.30^{a}	1.82^{a}	0.50^{abc}	1.99^{a}	2.49^{a}
T9	0.55^{ab}	1.33^{a}	1.88^{a}	0.53^{a}	2.10^{a}	2.63^{a}
T10	0.52^{ab}	1.28^{a}	1.80^{a}	0.52^{ab}	1.98^{a}	2.50^{a}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

Table 4.7 Effect of different treatments on N uptake by grain and straw of rice and wheat

	Rice			**Wheat**		
Treatment	**Straw N uptake (mg/pot)**	**Grain N uptake (mg/pot)**	**Total N uptake (mg/pot)**	**Straw N uptake (mg/pot)**	**Grain N uptake (mg/pot)**	**Total N uptake (mg/pot)**
T1	48.47 ^{d}	60.90 ^{d}	109.37 ^{d}	32.64 ^{e}	84.48 ^{d}	117.12 ^{d}
T2	83.81 ^{a}	110.22 ^{a}	194.03 ^{a}	55.46 ^{a}	160.57 ^{a}	216.03 ^{a}
T3	74.57 ^{b}	103.09 ^{bc}	177.66 ^{b}	49.04 ^{bc}	144.49 ^{bc}	193.52 ^{bc}
T4	62.88 ^{c}	89.73 c	152.61 ^{c}	43.21 ^{d}	123.12 ^{c}	166.33 ^{c}
T5	86.80 ^{a}	107.20 ^{ab}	194.00 ^{a}	54.90 ^{a}	154.53 ^{ab}	209.43 ^{ab}
T6	67.00 ^{c}	99.20 ^{bc}	166.20 ^{b}	46.08 ^{cd}	133.26 ^{c}	179.34 ^{c}
T7	84.73 ^{a}	110.01 ^{a}	194.74 ^{a}	54.11 ^{a}	158.88 ^{a}	213.00 ^{a}
T8	70.56 ^{bc}	99.06 ^{bc}	169.62 ^{b}	49.25 ^{bc}	139.30 ^{c}	188.55 ^{c}
T9	83.71 ^{a}	109.99 ^{a}	193.70 ^{a}	56.50 ^{a}	161.49 ^{a}	217.99 ^{a}
T10	70.41 ^{bc}	99.46 ^{bc}	169.86 ^{b}	51.84 ^{ab}	138.60 ^{c}	190.44 ^{c}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan's Multiple Range Test (DMRT).



(a) (b)

Figure 4.24 Relationship between grain yield and Nitrogen uptake by grain of (a) rice and (b) wheat

Table 4.8 Apparent recovery efficiency, agronomic efficiency and physiological efficiency of rice and wheat as influenced by different treatments

Treatment	**Rice**			**Wheat**		
	ARE(%)	**AE(g/g N)**	**PE (g/gN)**	**ARE(%)**	**AE(g/g N)**	**PE (g/gN)**
T1	0.00	0.00	0.00	0.00	0.00	0.00
T2	39.75^{c}	10.89^{g}	27.40^{abc}	46.44^{e}	13.19^{d}	28.41^{ab}
T3	42.68^{c}	11.88^{fg}	27.82^{abc}	47.75^{e}	13.63^{d}	28.53^{ab}
T4	50.09^{b}	12.90d^{ef}	25.75^{cd}	58.10^{cd}	15.70^{c}	27.02^{b}
T5	52.89^{ab}	12.69^{def}	23.99^{d}	57.69^{d}	17.81^{b}	29.41^{ab}
T6	53.11^{ab}	15.51^{ab}	29.21^{a}	58.15^{cd}	17.10^{bc}	30.88^{a}
T7	53.36^{ab}	13.63^{de}	25.53^{cd}	59.92^{cd}	17.56^{b}	29.31^{ab}
T8	56.31^{a}	14.86^{bc}	26.39^{bc}	66.75^{ab}	20.56^{a}	30.80^{a}
T9	52.71^{ab}	14.00^{cd}	26.56^{bc}	63.04^{bc}	18.06^{b}	28.65^{ab}
T10	56.54^{a}	16.26^{a}	28.76^{ab}	68.52^{a}	20.56^{a}	30.01^{a}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan's Multiple Range Test (DMRT).

4.12). While, at harvest of the crop (105 DAT), the mean value of NO_3^--N in soil ranged from 2.03 in T_1 to 2.97 mg kg^{-1} in T_2. It was also observed that lower level of fertilizers as T_6, T_8 and T_{10} were equally or more effective in maintaining availability of NO_3^--N content in soil during the later stages of crop growth, as higher level of fertilizer in conventional form (T_3).

4.3.7.3 Total mineral N (NH_4^+- N + NO_3^- -N) in rice

Total mineral N in soil was significantly affected by application of various fertilizer treatments. Compared to control (T_1) significantly higher amount of total mineral N was observed under all other treatments throughout the growing period. Highest content of total mineral N in soil was noticed under T_2 and T_5, T_7 and T_9 remained at par at most of the sampling dates. At 3 DAT, the mean value of mineral-N content in soil ranged from 22.01 mg kg^{-1} soil in T_1 to 40.67 mg kg^{-1} in T_2 (Table 4.13). While, at harvest of the crop (105 DAT), the mean value of mineral-N in soil ranged from 3.06 mg kg^{-1} in T_1 to 5.18 mg kg^{-1} in T_7. It was also observed that lower level of fertilizer as T_6, T_8 and T_{10} maintained same or even higher amount of total mineral N availability as under higher level of conventional fertilizer (T_3).

4.3.8 Soil NH_4 and NO_3 content in wheat

4.3.8.1 NH_4^+-N

Application of different fertilizer treatments significantly influenced ammonium N in soil during the wheatcrop growth periods. The NH_4^+-N content of soil under wheat was higher in soil fertilized with urea and other NCPCs compared to that of the no-N control treatment (Table 4.14). In general the NH_4^+- N content in soil decreased with the advancement of crop growth and become lowest at the time of harvest. The NH_4^+ -N content in soil showed three peaks, which appeared after urea applications. At 3 DAS, the mean value of NH_4^+ content in soil ranged from 9.89 mg kg^{-1} soil in T_1 to 22.10 mg kg^{-1} in T_2 (Table 4.14). While, at harvest of the crop (130 DAS), the mean value of NH_4^+ -N in soil ranged from 1.31 in T_1 to 3.18 mg kg^{-1} in T_5. Initially there is less soil remaining nitrogen in all treatments of the slow-release fertilizers compared with the accustomed fertilization application. Significantly higher amount of NH_4^+ -N content was observed in T_2 because of fast urea hydrolysis. The content of NH_4^+ -N in soil in T_7 remained almost at par with T_9 across the growing period. There is a sharp increase of soil N concentration after fertilizer application and a significant decline during the period of maximum N crop absorption. Among the three NCPCs, WF NCPC (@ 75 and 50 % RDF) maintained highest soil ammonium up to 40 DAS because of quick release of ammonium through hydrolysis and fast degradation in soil. Whereas, both Na-Alg and AA+Am NCPC (@ 75 and 50 % RDF) initially maintained less amount of NH_4^+ -N in soil due to slow release of the ammonium and maximum N absorption by the crops.

4.3.8.2 NO_3^- content

Among the fertilized treatments, the NO_3^--N content was highest in T_2 throughout the study period due to quick release of ammonium and its subsequent nitrification. In general, the content of NO_3^--N in soil decreased with advancement of crop growth due to absorption by the crops and became lowest at harvest of the crop (130 DAS). Unlike the NH_4^+-N content in wheat, the level of NO_3^--N in soil was lower in the T_7 and T_9 as compared to T_2 across the entire crop growing period. The NO_3^--N content under T_5 and T_2 remained at par on 10, 20, 40, 50 and 80 DAS. Soil nitrate content increased after split applications of urea and NCPCs. The NO_3^--N content under all the treatments were significantly higher over control (T_1) throughout the growing period (Table 4.15). At later stages of crop growth the content of NO_3^--N in soil at lower level of fertilizer (T_6, T_8 and T_{10}) application exhausted after 80 DAS (Table 4.15). At 3 DAS, the mean value of NO_3^--N content in soil ranged from 11.20 mg kg^{-1} in T_1 to 23.51 mg kg^{-1} soil in T_2 (Table 4.15). While, at harvest of the crop (130 DAS), the mean value of NO_3^--N in soil ranged from 1.8 mg kg^{-1}in T_1 to 5.15 mg kg^{-1} in T_5. It was also observed that during the initial stages of crop growth (up to 20 DAS) the rate of decrease of NO_3^--N in soil under T_2, T_3 and T_4 (conventional fertilizers) was much higher than under NCPCs containing treatments. It was also observed that lower level of fertilizers as T_6, T_8 and T_{10} were equally effective in maintaining availability of NO_3^--N content in soil as higher level of fertilizer in conventional form (T_3).

4.3.8.3 Total mineral N (NH_4^+- N + NO_3^- -N) in wheat

Total mineral N in soil was significantly affected by application of various fertilizer treatments. Compared to control (T_1) significantly higher amount of total mineral N was observed under all other treatments throughout the growing period (Table 4.16). Significantly higher content of total mineral N in soil was noticed under T_2 over all other treatments. It was observed that lower level of fertilizer as T_6, T_8 and T_{10}

Table 4.9 Micronutrient concentration in grain of rice and wheat as influenced by different treatments

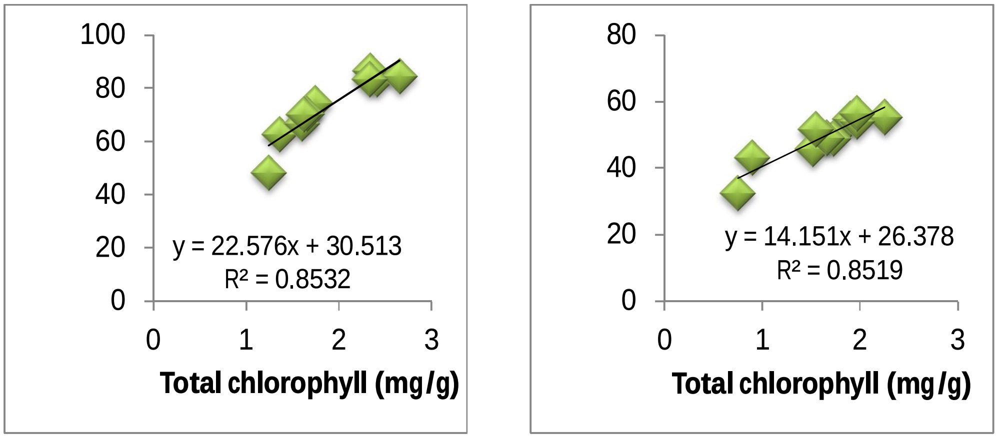
Treatment	**Rice**				**Wheat**			
	Fe (mg kg^{-1})	**Zn** (mg kg^{-1})	**Cu** (mg kg^{-1})	**Mn** (mg kg^{-1})	**Fe** (mg kg^{-1})	**Zn** (mg kg^{-1})	**Cu** (mg kg^{-1})	**Mn** (mg kg^{-1})
T1	19.31^{d}	26.50^{d}	1.14^{e}	24.10^{d}	37.00^{d}	35.20^{c}	4.82^{e}	36.07^{b}
T2	28.82^{a}	29.60^{abc}	1.87^{b}	33.24^{a}	41.20^{abcd}	40.00^{ab}	6.20^{bc}	41.01^{a}
T3	24.5^{bc}	27.40^{bcd}	1.64^{c}	28.70^{bc}	39.60^{abcd}	39.11^{abc}	5.70^{cd}	37.23^{ab}
T4	22.69^{c}	26.61^{cd}	1.28^{ef}	26.52^{cd}	37.30^{cd}	35.70^{c}	5.07^{e}	36.53^{b}
T5	26.37^{ab}	30.50^{a}	1.84^{b}	30.59^{ab}	41.40^{abc}	40.40^{ab}	6.52^{ab}	39.34^{ab}
T6	22.8^{c}	28.40^{abcd}	1.32^{e}	29.1^{bc}	38.20^{bcd}	37.70^{bc}	5.04^{e}	38.27^{ab}
T7	27.03^{a}	30.80^{a}	2.04^{a}	31.18^{ab}	43.60^{a}	41.90^{a}	6.88^{a}	41.00^{a}
T8	22.97^{c}	28.73^{abcd}	1.48^{d}	28.93^{bc}	39.30^{bcd}	38.20^{abc}	5.34^{de}	38.87^{ab}
T9	27.5^{a}	30.30^{ab}	1.98^{ab}	31.7^{ab}	42.20^{ab}	41.60^{ab}	7.02^{a}	41.10^{a}
T10	23.68^{c}	28.64^{abcd}	1.50^{cd}	29.54^{b}	39.50^{abcd}	38.70^{abc}	5.23^{de}	38.12^{ab}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

Table 4.10 Chlorophyll content of rice and wheat as influenced by different treatments

Treatment	Rice			Wheat		
	Chlorophyll a	Chlorophyll b	Total chlorophyll	Chlorophyll a	Chlorophyll b	Total chlorophyll
T1	0.68^{e}	0.56^{e}	1.24^{e}	0.50^{f}	0.25^{g}	0.75^{f}
T2	1.50^{a}	0.91^{d}	2.41^{a}	1.50^{a}	0.75^{a}	2.25^{a}
T3	0.98^{c}	0.76^{c}	1.74^{c}	1.23^{c}	0.50^{d}	1.73^{c}
T4	0.86^{d}	0.70^{d}	1.36^{e}	0.60^{f}	0.30^{f}	0.90^{e}
T5	1.32^{b}	1.02^{b}	2.34^{b}	1.30^{bc}	0.60^{c}	1.90^{b}
T6	0.90^{cd}	0.70^{d}	1.60^{d}	1.10^{e}	0.42^{e}	1.52^{d}
T7	1.42^{a}	1.24^{a}	2.66^{a}	1.32^{bc}	0.65^{b}	1.97^{b}
T8	0.94^{cd}	0.71^{d}	1.65^{d}	1.21^{cd}	0.45^{e}	1.66^{cd}
T9	1.31^{a}	1.02^{b}	2.33^{a}	1.35^{b}	0.62^{bc}	1.97^{b}
T10	0.92^{cd}	0.70^{d}	1.62^{d}	1.12^{de}	0.43^{e}	1.55^{d}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan's Multiple Range Test (DMRT).



(a) (b)

Figure 4.25 Relationship between chlorophyll content and straw N uptake of (a) rice and (b) wheat

Table 4.11 NH_4^+-N contents in soil under rice with different fertilizer treatments

Treatments	**3 day**	**10 day**	**20 day**	**33 day**	**40 day**	**50 day**	**63 day**	**80 day**	**105 day**
T1	12.79^{d}	8.80^{f}	7.57^{e}	8.01^{e}	6.98^{f}	5.38^{f}	4.56^{i}	4.17^{e}	1.03^{d}
T2	27.94^{a}	19.90^{a}	13.72^{b}	20.94^{a}	13.17^{a}	9.25^{b}	17.53^{a}	9.10^{b}	2.19^{b}
T3	21.40^{b}	16.50^{d}	10.21^{cd}	18.07^{b}	8.04^{de}	7.89^{c}	14.50^{cd}	7.73^{c}	2.01^{b}
T4	18.36^{c}	15.53^{c}	8.84^{de}	12.16^{cd}	7.19^{f}	6.16^{e}	11.90^{fg}	6.19^{d}	1.53^{c}
T5	23.31^{b}	18.79^{b}	14.01^{ab}	17.70^{c}	10.18^{c}	9.04^{b}	16.30^{ab}	9.03^{b}	2.15^{b}
T6	17.87^{c}	13.58^{d}	8.52^{cd}	11.91^{d}	8.06^{de}	8.12^{c}	12.60^{ef}	8.92^{b}	2.12^{b}
T7	18.17^{c}	18.30^{b}	14.69^{ab}	17.31^{c}	11.79^{b}	9.43^{b}	15.20^{bc}	10.13^{a}	2.38^{a}
T8	17.50^{c}	14.90^{c}	8.92^{c}	11.47^{d}	8.26^{d}	7.16^{d}	11.10^{gh}	8.80^{b}	2.09^{b}
T9	17.91^{c}	18.42^{b}	15.30^{a}	17.41^{c}	12.43^{ab}	10.08^{a}	13.43^{de}	10.42^{a}	2.42^{a}
T10	16.07^{c}	14.57^{d}	8.50^{c}	11.04^{c}	9.70^{c}	7.04^{d}	10.16^{h}	8.99^{b}	2.08^{b}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

Table 4.12 NO_3^-–N contents in soil under rice with different fertilizer treatments

Treatments	**3 day**	**10 day**	**20 day**	**33 day**	**40 day**	**50 day**	**63 day**	**80 day**	**105 day**
T1	7.80^{e}	6.45^{f}	5.30^{c}	6.10^{f}	5.90^{e}	5.41^{h}	5.30^{e}	5.02^{f}	2.03^{c}
T2	12.73^{a}	13.90^{a}	10.29^{a}	15.37^{a}	12.60^{a}	9.12^{a}	13.51^{a}	8.70^{bc}	2.97_{a}
T3	10.53^{bc}	10.97^{c}	9.42^{a}	13.73^{d}	8.07^{cd}	6.52^{g}	12.34^{cd}	5.96^{e}	2.24^{bc}
T4	9.86^{cd}	8.03^{d}	7.28^{b}	10.28^{e}	7.68^{d}	5.63^{h}	7.04^{d}	5.13^{f}	2.31^{b}
T5	10.44^{bc}	10.08^{c}	9.34^{a}	13.40^{b}	10.50^{a}	8.90^{ab}	12.75^{ab}	9.20^{a}	2.13^{bc}
T6	8.50^{de}	7.85^{d}	7.19^{b}	10.47^{e}	8.12^{cd}	7.90^{de}	8.34^{c}	7.16^{d}	2.21^{bc}
T7	9.70^{cd}	10.40^{c}	9.71^{a}	12.98^{bc}	10.76^{b}	8.30^{cd}	11.93^{b}	8.31^{c}	2.8^{a}
T8	8.90^{cde}	7.43^{de}	6.97^{b}	10.61^{e}	8.70^{c}	7.31^{f}	8.00^{cd}	7.84^{c}	2.17^{bc}
T9	9.29^{cde}	11.30^{b}	9.60^{a}	12.01^{cd}	10.40^{b}	8.50^{bc}	12.04^{b}	8.54^{bc}	2.02^{c}
T10	8.32^{de}	7.12^{e}	6.58^{b}	9.83^{e}	8.82^{c}	7.50^{ef}	8.11^{cd}	7.89^{c}	2.16^{bc}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

maintained same or even higher amount of total mineral N availability as under higher level of conventional fertilizer (T_3).

4.3.9 Nitrification rate in rice and wheat soil

Nitrification rate was measured by the formula given by Sahrawat (1980). Nitrite-N content was found insignificant (<0.5 ppm) throughout the experiment in all of the treatments, therefore not considered. Overall mean of NH_4^+ and NO_3^- -N of all the treatments measured throughout the rice and wheat growing periods were calculated to obtain nitrification rate. Lower nitrification rate was observed in NCPCs treated soil compared to conventional fertilizers in both rice and wheat soils (Figure 4.26). In rice crop lowest nitrification rate was observed in T_9 (44.84%) and highest was observed in T2 (48.32%). In wheat highest nitrification rate was seen in T_2 (54.99%) and lowest in T_{10} (49.16%).

4.3.10 Partial nitrogen balance in rice and wheat crops

Partial N balanceat crop harvest was determined based on the total soil mineral N content before crop seeding, soil mineral N remained at crop harvest, total N uptake by the crop (straw + grain), and total amount of N added from fertilizer during the crop growing period. The N input was calculated by adding the initial soil mineral N content and the amount of N from added N fertilizer (Liu *et al*., 2003). Similarly, N output was calculated by adding plant uptake to the mineral N content remained in the soil.

At rice harvest highest percentage (40.4%) of unaccounted mineral N was recorded in T_2 (100% N RDF) as shown in Figure 4.27. When nitrogen fertilizer was applied at 75% of RDF maximum loss was observed in T_3 of 27.4%, whereas highest unaccounted mineral nitrogen percentage was observed in 50% N fertilized T_4 treatment (9.2%). At wheat harvest 25.7% of mineral N was unaccounted (lost) in T_2 (Figure 4.28). Whereas, when fertilizer was applied at 75% RDF, the highest unaccounted mineral N was 17.0% (T_3), in case of 50% applied fertilizer 7.8% of mineral N was uncounted in T_4. All NCPC fertilizers significantly reduced the percentage of unaccounted mineral N than conventional fertilizer in both rice and wheat crops.

4.3.11 Total nitrogen

Application of different treatments significantly increased the TN content in rice crop soil as compared to control (T_1). Treatments T_2 (0.49g kg^{-1}), T_5 (0.47 g kg^{-1}), T_7 (0.49 g kg^{-1}) and T_9 (0.51 g kg^{-1}) were significantly at par (Table 4.17). All the treatments applied @ 50% N through NCPCs showed significantly better results than same amount of N applied through urea (T_4) and these treatments were equally better as T_3.

The data on total N (TN) in soil revealed a significant effect of treatments (Table 4.17). The values ranged from 0.28 g kg^{-1}in control (T_1) to 0.46 g kg^{-1} in 100% NPK (T_2) in wheat after harvesting. Application of AA+Am NCPC @ 75% N of RDF (0.43 g kg^{-1}) was as good as 100% N through urea, and both treatments were significantly better. Other treatments T_5 (0.42g kg^{-1}) and T_7 (0.41g kg^{-1}) also showed no significant difference with T_9 with respect to TN content in soil.Treatments applied at 50% N through NCPCs (T_6, T_8 and T_{10}) were significantly at par with T_3 (75% N by urea).

4.3.12 Soil organic carbon

Addition of conventional fertilizer and NCPCs at higher dose resulted in significantly ($p < 0.05$) higher organic carbon in soil than control in rice after harvesting (Table 4.17). The mean OC content in soil varied from 3.45 g kg^{-1} in control (T_1) to 4.12 g kg^{-1}in T9. Data revealed that application of conventional fertilizer alone @ 100% RDF did not improve the OC content in soil over treatment (T_9). However, application of Na-Alg NCPC @ 75% RDF found to maintain significantly equal higher OC as T_9. Similarly all the treatments of NCPCs @ 50% of RDF showed equal effect on OC content with treatment T_3 and T_4.

Similarly OC content in soil was significantly ($p < 0.05$) influenced due to different treatment application in wheat (Table 4.17). The mean OC content in soil varied from 3.38 g kg^{-1} in control (T_1) to 3.96 g kg^{-1} in T_9. The highest OC value was recorded in T_9 (3.96 g kg^{-1}) followed by T_7 (3.88 g kg^{-1}) and T_5 (3.62 g kg^{-1}) and remained statistically at par.

4.3.13 Microbial biomass carbon

The microbial biomass carbon content of soil was determined after harvest of each crop and data pertaining to microbial biomass carbon (MBC) content in soil as

Table 4.13 Mineral–N contents in soil under rice with different fertilizer treatments

Treatments	**3 day**	**10 day**	**20 day**	**33 day**	**40 day**	**50 day**	**63 day**	**80 day**	**105 day**
T1	22.01^{d}	15.25^{g}	12.87^{d}	14.11^{e}	12.88^{g}	10.79^{e}	9.86^{f}	9.19^{g}	3.06^{d}
T2	40.67^{a}	33.80^{a}	24.01^{a}	36.31^{a}	25.77^{a}	18.37^{a}	31.04^{a}	17.80^{bc}	5.16^{a}
T3	31.93^{b}	27.47^{c}	19.63^{b}	31.80^{c}	16.11^{ef}	14.41^{d}	26.84^{d}	13.69^{e}	4.25bc
T4	28.22^{c}	23.56^{f}	16.12^{c}	22.44^{d}	14.87^{f}	11.79^{e}	18.94^{e}	11.32^{f}	3.84c
T5	33.75^{b}	28.87^{b}	23.35a	31.1^{b}	20.68^{b}	17.94^{b}	29.05^{c}	18.23^{b}	4.55b
T6	26.37^{c}	21.43^{e}	15.71^{c}	22.38^{c}	16.18^{ef}	16.02^{c}	20.94^{d}	16.08^{d}	4.33b
T7	27.87^{c}	28.70^{a}	24.4^{a}	30.29^{b}	22.55^{b}	17.73^{b}	27.13^{bc}	18.44^{ab}	5.18^{a}
T8	26.4^{c}	22.33^{cd}	15.89^{bc}	22.08^{c}	16.96^{de}	14.47^{d}	19.10^{e}	16.64^{d}	4.26^{bc}
T9	27.20^{c}	29.72^{b}	24.9a	29.42^{b}	22.83^{c}	18.58^{b}	25.47^{b}	18.96^{a}	4.17^{bc}
T10	24.39^{c}	21.69^{de}	15.08^{c}	20.87^{c}	18.52^{d}	14.54^{d}	18.27^{e}	16.88^{cd}	4.25^{bc}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

Table 4.14 NH_4^+-N contents in soil under wheat with different fertilizer treatments

Treatments	**3 day**	**10 day**	**20 day**	**33 day**	**40 day**	**50 day**	**63 day**	**80 day**	**130 day**
T1	9.89^{e}	7.76^{f}	5.40^{f}	7.12^{f}	4.80^{f}	5.02^{f}	4.20^{e}	4.30^{g}	1.31^{f}
T2	22.10^{a}	12.50^{a}	9.61^{a}	16.20^{a}	12.70^{a}	8.83^{b}	13.85^{a}	7.61^{cd}	2.87^{b}
T3	19.31^{b}	11.50^{b}	7.92^{cd}	12.60^{c}	8.03^{d}	6.31^{e}	10.51^{c}	6.78^{e}	2.13^{cd}
T4	15.90^{cd}	9.60^{d}	6.59^{e}	8.98^{e}	6.91^{e}	5.57^{f}	8.70^{d}	5.63^{f}	2.09^{cd}
T5	18.10^{bc}	11.91^{ab}	9.11^{ab}	14.21^{b}	10.89^{b}	7.36^{d}	12.60^{b}	7.05^{de}	3.18^{a}
T6	14.20^{d}	8.81^{e}	7.72^{d}	10.90^{d}	8.89^{c}	7.12^{d}	10.61^{c}	7.93^{c}	2.96^{b}
T7	16.07^{cd}	10.50^{c}	8.23^{bcd}	11.45^{d}	10.29^{b}	12.16^{a}	12.90^{ab}	9.96^{a}	2.30^{c}
T8	15.40^{cd}	8.27^{ef}	7.80^{d}	9.44e	8.72^{cd}	7.94^{c}	10.32^{c}	7.83^{c}	1.98^{cd}
T9	16.28^{cd}	10.23^{cd}	8.90^{abc}	11.16^{d}	10.25^{b}	12.37^{a}	12.80^{ab}	8.92^{b}	2.12^{cd}
T10	14.80_{d}	8.15^{ef}	7.53^{de}	9.13^{e}	8.15^{cd}	8.60^{b}	10.30^{c}	7.90^{c}	1.81^{e}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan's Multiple Range Test (DMRT).

Table 4.15 NO_3^- –N contents in soil under wheat with different fertilizer treatments

Treatments	3 day	10 day	20 day	33 day	40 day	50 day	63 day	80 day	130 day
T1	11.20^{f}	8.95^{d}	6.75^{e}	7.61^{e}	6.76^{f}	6.13^{e}	5.53^{f}	5.10^{f}	1.8^{f}
T2	23.51^{a}	17.30^{a}	12.90^{a}	20.25^{a}	15.03^{a}	10.31^{a}	16.65^{a}	9.14^{ab}	3.86^{b}
T3	18.83^{b}	13.20^{b}	9.28^{c}	16.70^{b}	12.81^{d}	7.92^{c}	14.44^{b}	7.27^{d}	3.35^{c}
T4	17.12^{bc}	10.07^{c}	7.50^{e}	12.95^{c}	8.98^{de}	7.87^{c}	10.43^{d}	6.93^{d}	1.66^{f}
T5	18.10^{b}	12.50^{b}	9.79^{ab}	14.50^{b}	11.31^{d}	10.18^{ab}	14.40^{b}	9.54^{a}	5.15^{a}
T6	13.18^{de}	11.78^{b}	8.20^{d}	11.40^{d}	9.32^{d}	8.10^{c}	9.05^{e}	7.59^{d}	3.83^{b}
T7	15.01^{cd}	12.25^{b}	10.39^{bc}	13.89^{bc}	12.52^{bc}	9.80^{ab}	13.76^{b}	8.28^{c}	3.02^{d}
T8	12.92^{de}	10.70^{c}	8.51^{cd}	11.60^{d}	9.50^{d}	8.31^{c}	8.80e	6.25^{e}	1.90^{f}
T9	14.98^{cd}	12.27^{b}	10.56^{b}	13.83^{bc}	12.73^{c}	9.62^{b}	13.27^{bc}	8.78^{bc}	2.59^{e}
T10	12.19^{ef}	10.92^{c}	8.57^{cd}	10.62^{d}	8.20^{e}	6.84^{d}	8.24^{e}	7.04^{d}	1.84^{f}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

influenced by application of different treatments are presented in Table 4.18. In case of rice, addition of 100% RDF treatment (T_2) equally improves the mean microbial biomass C with T_5. Significant increase in MBC in soil was observed due to application of 75% Urea RDF (T_3) which remained insignificant with the treatments receiving 50% RDF through NCPCs (T_6, T_8 and T_{10}). Significantly ($p < 0.05$) highest MBC in soil (131.48 mg kg^{-1}) was maintained in treatment T_5 and at par with the treatment T_2, T_7 and T_9.

Results revealed that addition of fertilizer treatments significantly ($p< 0.05$) increased microbial biomass carbon than control in wheat (Table 4.18). The mean values of microbial biomass C in soil ranged from 81.9 mg kg^{-1} (T_1) to 120.23 mg kg^{-1} (T_7), the latter being significantly higher than rest of the treatments in wheat crop except T_2, T_3, T_7 and T_9.

4.3.14 Microbial biomass nitrogen

Microbial biomass N in soil had shown a significant ($p < 0.05$) effect due to application of different fertilizers (Table 4.18). In rice, the mean value of MBN in different treatments varied from 16.46 mg kg^{-1} (T_1) to 30.32 mg kg^{-1} (T_5). The results in Table 4.19 revealed that MBN content in soil was significantly influenced by application of degradable NCPCs. Application of WF NCPC at 75% RDF significantly increase the MBN content than others and the second best treatment was T_9 (29.09 mg kg^{-1}). Similarly, third best treatment T_2 (28.24 mg kg^{-1}) to wheat did not differ significantly from T_5. All the treatments, were significantly superior to control (T_1) in increasing MBN content in soil.

Data revealed that the mean microbial biomass N in wheat soil under T_5 (23.8 mg kg^{-1}) and T_9 (22.9 mg kg^{-1}) were significantly superior over control T_1 (15.11 mg kg^{-1}) as well as other treatments (Table 4.18). It was also evident that application of NCPCs at 50% RDF (T_6, T_8 and T_{10}) significantly increased the MBN in soil over T_1. The data have revealed that treatment having conventional fertilizer at 75% RDF i.e. T_3, T_6, T_8 and T_{10} did not differ significantly. The following order in terms of MBN content in soils under different treatments is given below:

$$T_5>T_9> T_2>T_7>T_3>T_8>T_{10}>T_6 >T_4 > T_1$$

The Soil microbial biomass C as percentage of the SOC content in wheat accounted for 2.42% in control to 3.32% in T_5 and in rice 2.30% (T_1) to 3.59% in T_5

and the microbial biomass N contributed 4.72% (T_2) to 5.67% (T_5) in wheat and 5.21% (T_{10}) to 6.45% (T_5) to total N in rice (Table 4.18).The mean soil microbial biomass C/N values after harvesting in rice and wheat season ranges from 4 - 4.82 and 5 - 5.74, respectively (Table 4.18).

4.3.15 The urease activity

Data revealed that application of different fertilizer treatments significantly influenced the urease activity in rice (Table 4.20). Significantly highest mean urease activity in soil (9.84 μg urea g^{-1} h^{-1}) was found in T_5 compared to rest of the treatments (Figure 4.31). Sole application of conventional fertilizer as well as biodegradable NCPCs showed significantly higher urease activity in soil as compared to control (5.60 μg urea g^{-1} h^{-1}).

The urease activity in wheat with N fertilization was significantly higher than that of control (T_1), (Table 4.20).Application of biodegradable NCPCs in combination with urea at different levels resulted in significant increase in urease activity over control (4.45 μg urea g^{-1} h^{-1}). Significantly highest mean urease activity in soil (7.43 μg urea g^{-1} h^{-1}) was found in T_5 followed by T_7 (6.21 μg urea g^{-1} h^{-1}), T_2 (5.97 μg urea g^{-1} h^{-1}) and T_9 (5.88 μg urea g^{-1} h^{-1}). It was also noticed that application of biodegradable NCPCs along with 75% N RDF (T_5 and T_7) was found to maintain significantly higher urease activity in soil than treatment receiving only conventional fertilizer (T_3). Further, no significant differences were noticed among the treatments T_3, T_4, T_6, T_8 and T_{10}.

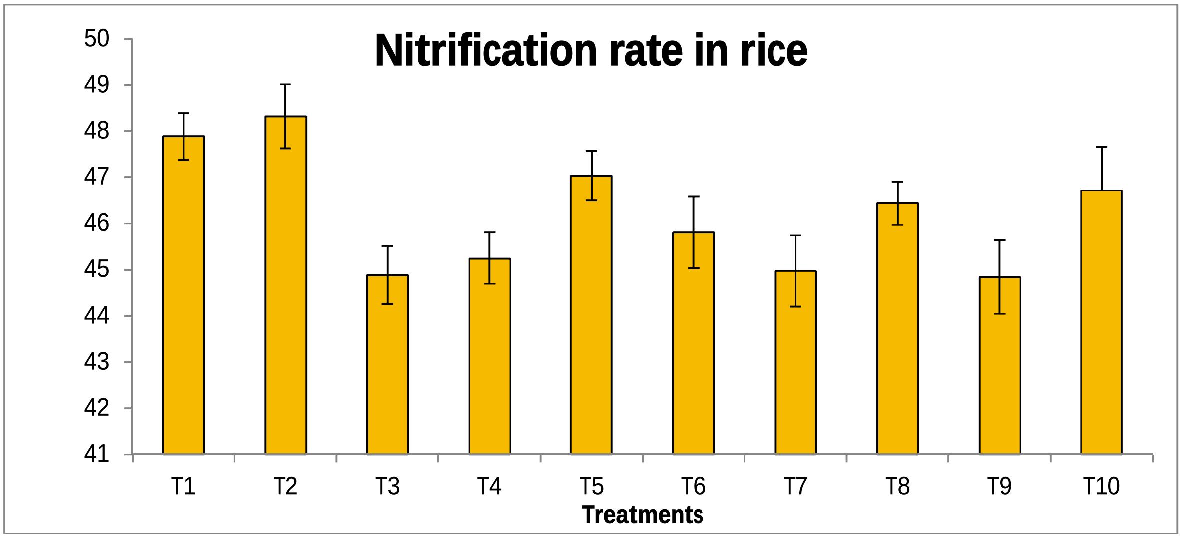
4.3.16 Dehydrogenase activity

Data on dehydrogenase activity in soil as influenced by different fertilizer treatments in rice and wheat are presented in Table 4.20. Significant increase in dehydrogenase activity in soil was noticed due to application of urea and NCPCs as compared to control treatment in rice (Table 4.20). The treatment T_5 was found to exhibit significantly higher dehydrogenase activity (46.19 μg TPF g^{-1} h^{-1}) followed by T_7 (41.15 μg TPF g^{-1} h^{-1}), T_2 (31.56 μg TPF g^{-1} h^{-1}) and T_9 (27.12 μg TPF g^{-1} h^{-1}). Though the significant increase in dehydrogenase activity in soil under treatments like T_6, T_8 and T_{10} compared to T_4 was observed, but the differences were insignificant among these treatments (T_6, T_8 and T_{10}) (Figure 4.31).

Table 4.16 Mineral –N contents in soil under wheat with different fertilizer treatments

Treatments	3 day	10 day	20 day	33 day	40 day	50 day	63 day	80 day	130 day
T1	21.09^{e}	16.71^{d}	12.15^{e}	14.73^{f}	11.56^{f}	11.15^{f}	9.73^{e}	9.40^{g}	3.11^{f}
T2	45.61^{a}	29.80^{a}	22.51^{a}	36.45^{a}	27.73^{a}	19.14^{b}	30.50^{a}	16.75^{bc}	6.73^{b}
T3	38.14^{b}	24.70^{b}	17.20^{d}	29.30^{b}	20.84^{d}	14.23^{e}	24.91^{c}	14.05^{e}	5.48^{c}
T4	33.02^{bc}	19.67^{c}	14.09^{e}	21.93^{de}	15.89^{e}	13.44^{d}	19.13^{d}	12.56^{f}	3.75^{e}
T5	36.20^{b}	24.41^{b}	18.90^{bc}	28.71^{b}	22.20^{c}	17.54^{c}	27.00^{b}	16.59^{bc}	8.33^{a}
T6	27.38^{d}	20.59^{c}	15.92^{de}	22.30^{d}	18.21^{d}	15.22^{d}	19.66^{d}	15.52^{cd}	6.79^{b}
T7	31.08^{cd}	22.75^{b}	18.62^{bc}	25.34^{c}	22.81^{c}	21.96^{a}	26.66^{b}	18.24^{a}	5.32^{c}
T8	28.32^{cd}	18.97^{c}	16.31^{d}	21.04^{de}	18.22^{d}	16.25^{cd}	19.12^{d}	14.08^{e}	3.88^{e}
T9	31.26^{cd}	22.50^{b}	19.46^{ab}	24.99^{c}	22.98^{c}	21.99^{a}	26.07^{b}	17.70^{ab}	4.71^{d}
T10	26.99^{d}	19.07^{c}	17.10^{d}	19.75^{e}	16.35^{de}	15.44^{d}	18.54^{d}	14.94^{de}	3.65^{e}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).



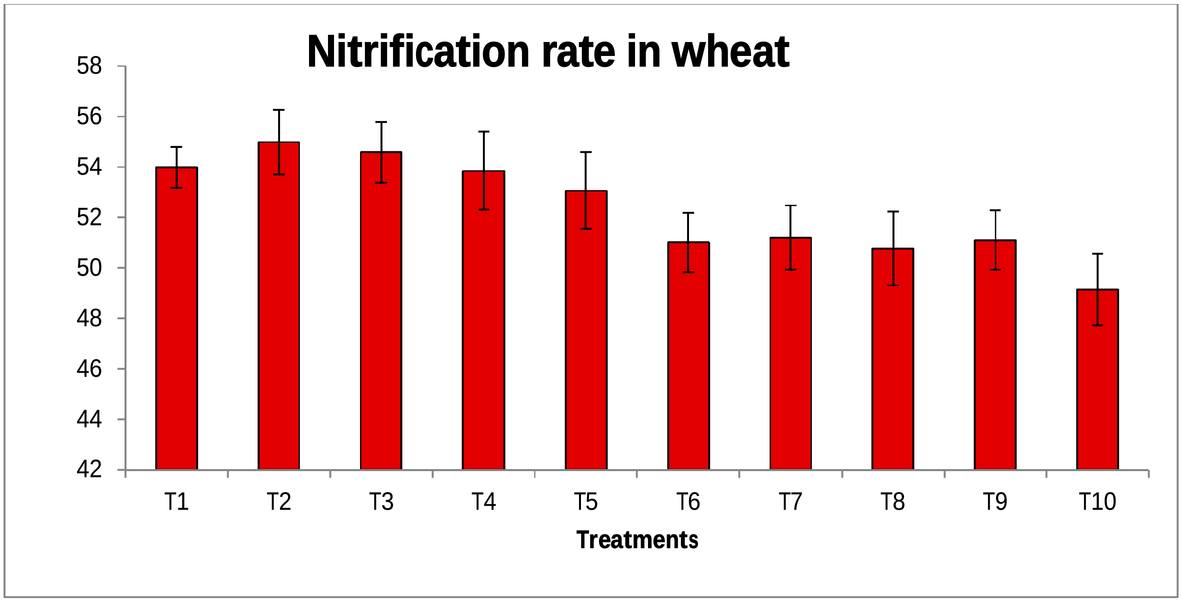


Figure 4.26 Average nitrification rate in rice and wheat crop soil influenced by different treatments

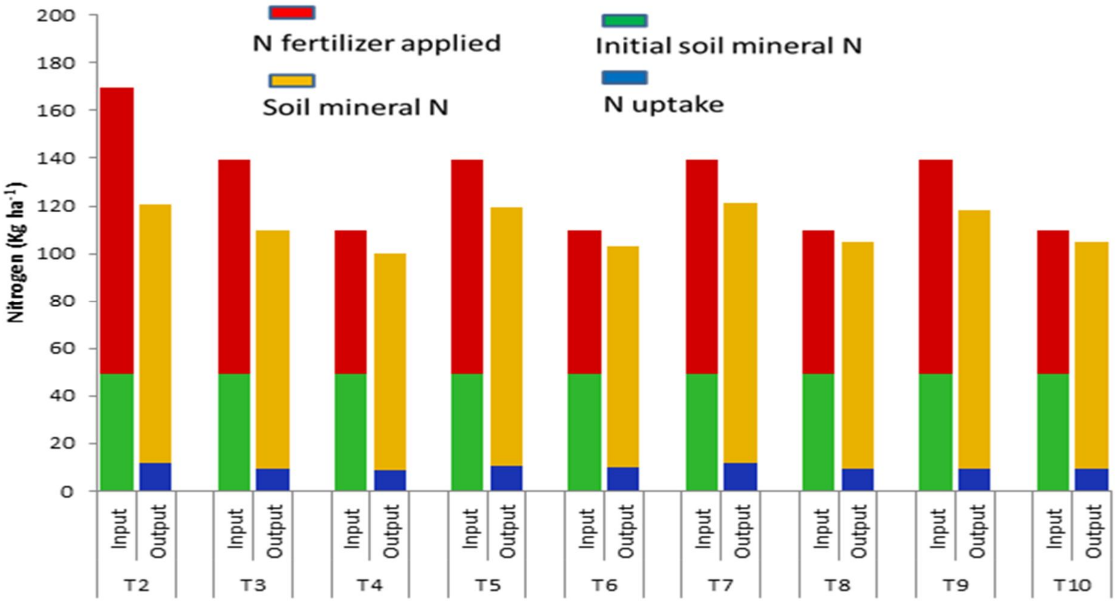


Figure 4.27 Partial N balance in rice soil influenced by different treatments

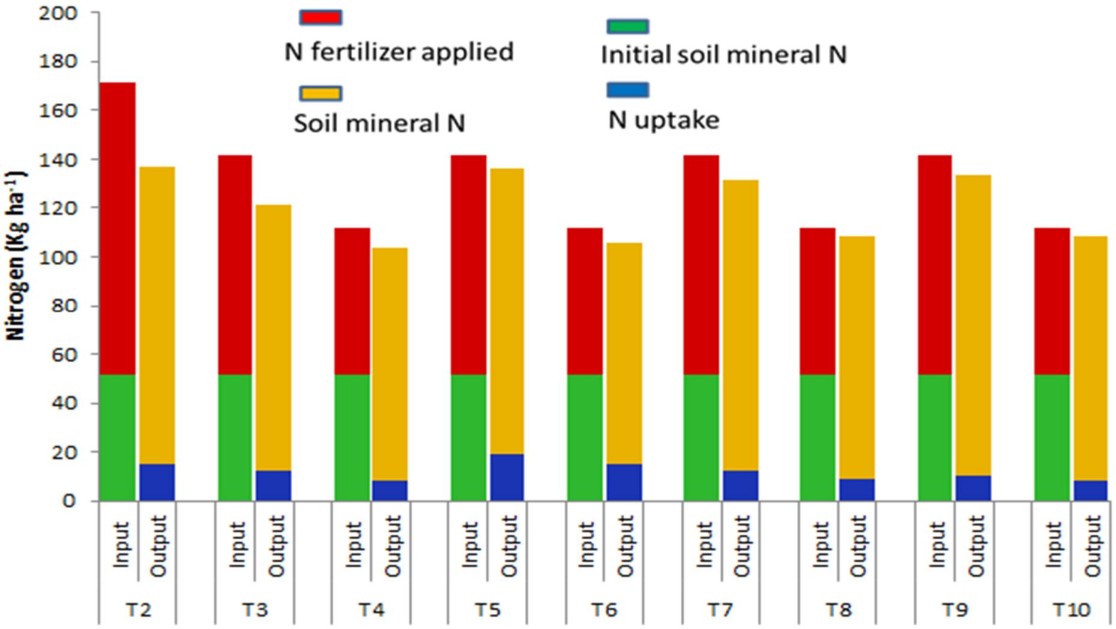


Figure 4.28 Partial N balance in wheat soil influenced by different treatments

Table 4.17 Organic carbon (g kg^{-1}) and TN in rice and wheat crop soil after harvesting as affected by different treatments

Treatments	**SOC (g kg^{-1})**		**TN (g kg^{-1})**		**SOC/TN (g C g N^{-1})**	
	Rice	Wheat	Rice	Wheat	Rice	Wheat
T1	3.45^{d}	3.38^{d}	0.27^{e}	0.28^{e}	12.77^{a}	12.07^{a}
T2	3.71^{bc}	3.68^{abc}	0.49^{ab}	0.46^{a}	7.57^{c}	8.00^{e}
T3	3.60^{c}	3.58^{bc}	0.43^{c}	0.37^{c}	8.37^{bc}	9.68^{bc}
T4	3.40^{cd}	3.32^{cd}	0.38^{d}	0.32^{d}	8.95^{b}	10.38^{ab}
T5	3.66^{c}	3.62^{abc}	0.47^{ab}	0.42^{b}	7.79^{c}	8.62^{de}
T6	3.53c	3.4^{cd}	0.44^{c}	0.35^{cd}	8.02^{bc}	9.71^{bc}
T7	4.03ab	3.88^{ab}	0.49^{ab}	0.41^{b}	8.22^{bc}	9.46^{bcd}
T8	3.54c	3.46^{c}	0.45^{bc}	0.34^{cd}	7.87^{c}	10.18^{abc}
T9	4.12a	3.96^{a}	0.51^{a}	0.43^{ab}	8.08^{bc}	9.21^{cd}
T10	3.58c	3.39^{cd}	0.45^{bc}	0.35^{cd}	7.96^{c}	9.69^{bc}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

Table 4.18 Effect of different fertilizer treatments on MBC (mg kg^{-1}) and MBN (mg kg^{-1}) in rice- wheat crops soil after harvesting

Treatments	**MBC**		**MBN**		**MBC/MBN**	
	Rice	**Wheat**	**Rice**	**Wheat**	**Rice**	**Wheat**
T1	79.37^{c}	81.9^{c}	16.46^{f}	15.11^{f}	4.82^{a}	5.42^{abc}
T2	126.78^{a}	118.02^{a}	28.24^{ab}	21.7^{b}	4.49^{bc}	5.44^{abc}
T3	107.32^{b}	112.14^{a}	26.8^{bc}	19.55^{cd}	4.00^{d}	5.74^{a}
T4	87.3^{c}	93.62^{b}	21.71^{e}	17.14^{e}	4.02^{d}	5.46^{abc}
T5	131.48^{a}	120.23^{a}	30.32^{a}	23.8^{a}	4.34^{bcd}	5.05^{c}
T6	100.45^{b}	97.34^{b}	23.63^{de}	18.34^{de}	4.25^{cd}	5.31^{abc}
T7	128.12^{a}	119.1^{a}	27.1^{bc}	21.3^{bc}	4.73^{ab}	5.59^{ab}
T8	108.7^{b}	98.9^{b}	24.95^{cd}	19.2^{d}	4.36^{bcd}	5.15^{bc}
T9	124.5^{a}	114.43^{a}	29.09^{ab}	22.9^{ab}	4.28^{bcd}	5.00^{c}
T10	99.1^{b}	95.18^{b}	23.44^{de}	18.8d^{e}	4.23^{cd}	5.06^{bc}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan's Multiple Range Test (DMRT).

Table 4.19 Percentage of MBC in SOC and MBN in TN after harvesting of rice and wheat

Treatments	**MBC as percentage soil C**		**MBN as percentage TN**	
	Rice	**Wheat**	**Rice**	**Wheat**
T1	2.30^{e}	2.42_{d}	6.10^{abc}	5.40^{a}
T2	3.42^{a}	3.21^{a}	5.76^{bcd}	4.72^{b}
T3	2.98^{bc}	3.13^{ab}	6.23^{ab}	5.28^{a}
T4	2.57^{de}	2.82^{bcd}	5.71^{bcd}	5.36^{a}
T5	3.59^{a}	3.32^{a}	6.45^{a}	5.67^{a}
T6	2.85^{cd}	2.86^{bcd}	5.37^{d}	5.24^{ab}
T7	3.18^{b}	3.07^{abc}	5.53^{cd}	5.20^{ab}
T8	3.07^{bc}	2.86^{bcd}	5.54^{cd}	5.65^{a}
T9	3.02^{bc}	2.89^{bcd}	5.70^{bcd}	5.33^{a}
T10	2.77^{d}	2.81^{cd}	5.21^{d}	5.37^{a}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

In succeeding wheat crop, results revealed that mean dehydrogenase activity in soil ranged from 7.14 µg TPF g^{-1} h^{-1}in control (T_1) to 20.37 µg TPF g^{-1} h^{-1} (T_7) in wheat among the different treatments (Table 4.20). In all the treatments dehydrogenase activity was significantly ($p< 0.05$) higher as compared to control (T_1). Application of WF NCPC (T_5) and Na-Alg NCPC (T_7) significantly increase the dehydrogenase activity in soil over conventional fertilizer (T_2). The dehydrogenase activity in wheat at 50% RDF applied treatments after harvesting showed significantly higher value in T_6 followed by T_{10} and T_8 as compared to T_3.

4.3.17 Acid phosphatase activity

Effect of fertilizer treatments were significant ($p <0.05$) regarding acid phosphatase activities in soil samples (Table 4.20). In rice crop maximum acid phosphatase activity was found in $T_5$with 99.31 µg of p-nitrophenol released g^{-1} h^{-1} (Figure 4.33). Application of NCPCs at 75% RDF resulted in a significant increase in acid phosphatase activity in T_7 (85.66 µg g^{-1} h^{-1}) and remained at par with T_2 (82.45 µg g^{-1} h^{-1}). Treatments having 50% of RDF in NCPCs (T_6 and T_{10}) remained at par with the control (T_1) and conventional fertilizer (T_4).

Acid phosphatase activity varied from 48.42 to 93.09 µg g^{-1} h^{-1} in the wheat season crop (Table 4.20). T_5 (93.09 µg g^{-1} h^{-1}) had maximum acid phosphatase activity followed by T_7 (90.23 µg g^{-1} h^{-1}) and T_2 (88.79 µg g^{-1} h^{-1}) (Figure 4.33).

4.3.18 Alkaline phosphatase activity

Alkaline phosphatase activity was found to be maximum in the treatment T_5 (159.81 µg g^{-1} h^{-1}) in rice crop and minimal in the control T_1 (80.66 µg g^{-1} h^{-1}) and showed the following trends (Figure 4.34):

T_5 (159.81 µg g^{-1} h^{-1}) > T_7 (146.65 µg g^{-1} h^{-1}) > T_2 (140.49 µg g^{-1} h^{-1}) > T_9 (120.5 µg g^{-1} h^{-1}) > T_3 (94.71 µg g^{-1} h^{-1}) > T_8 (91.63 µg g^{-1} h^{-1}) > T_{10} (90.34 µg g^{-1} h^{-1}) > T_6 (89.76 µg g^{-1} h^{-1}) > T_4 (87.32 µg g^{-1} h^{-1}) > T_1 (80.66 µg g^{-1} h^{-1}).

Mean values of the treatments in wheat (Table 4.20) for alkaline phosphatase activity varied from a minimum 73.8 µg g^{-1} h^{-1} in T_1 to maximum in the T_5 (123.49 µg g^{-1} h^{-1}). The treatment T_7 (117.1) was next best treatment followed by T_9 (110.65 µg g^{-1} h^{-1}). The data have revealed the following order in terms of alkaline phosphatase activity in soils under different treatments (Figure 4.34):

T_5 (123.49 µg g^{-1} h^{-1}) >T_7 (117.1 µg g^{-1} h^{-1}) > T_9 (110.65 µg g^{-1} h^{-1}) >T_2 (109.52 µg g^{-1} h^{-1}) > T_3 (92.27 µg g^{-1} h^{-1}) > T_6 (83.74 µg g^{-1} h^{-1}) > T_8 (80.62 µg g^{-1} h^{-1}) > T_{10} (77.9 µg g^{-1} h^{-1}) > T_4 (75.6 µg g^{-1} h^{-1}) > T_1 (73.8 µg g^{-1} h^{-1}).

4.3.19 Correlation matrix

Data on Pearson's correlation matrix in the present study (Table 4.22 and 4.23) showed that biomass yield of rice and wheat crop was significantly and positively correlated (P =0.01) with nitrogen uptake (r= 0.967) and (r= 0.858), respectively. The SOC and MBC are significantly correlated with yield and N uptake by rice and wheat. On the other hand SOC and MBC were significantly correlated with each other.

Similarly TN and mineral N relation with yield and uptake (Table 4.22 and 4.23) were found significant (P= 0.01). Both these pools of nitrogen significantly correlated with yield and N uptake. Mineral N, TN and MBN were significantly correlated (P=0.01) with each other. Dehydrogenase, phosphatase and urease activity were well correlated with yield and nutrients uptake by rice and wheat. All these enzymes were significantly correlated with organic pool of carbon and different nitrogen pools in rice, however, exception was noticed in wheat where acid phosphatase was not correlated significantly with SOC.

4.3.20 N_2O emissions in rice and wheat crop seasons

4.3.20.1 N_2O emissions in rice

In both the rice and wheat crop seasons, daily N_2O fluxes and total emissions were significantly affected by various treatments. Emission of N_2O-N ranged from 3.94 to 10.53 g ha^{-1} day^{-1} during 65 days of the experiment in rice (Figure 4.35). Denitrification of nitrate in anaerobic soil condition was presumably responsible for the formation of N_2O. A peak of N_2O-N was observed on the 2nd day after application of urea and different NCPCs. High emission of N_2O on day 2 in all the treatments was due to formation of N_2O during nitrification of ammonium N already present in soil as well as ammonium N produced by the hydrolysis of urea. Three peaks of N_2O-N emission were observed on 3, 33-34 and 63-64 DAT / DAS in urea treatment during 65 days (in case of rice) and 70 days (in case of wheat) of the experiment coinciding with the splits of N applied followed by a decline to reach a

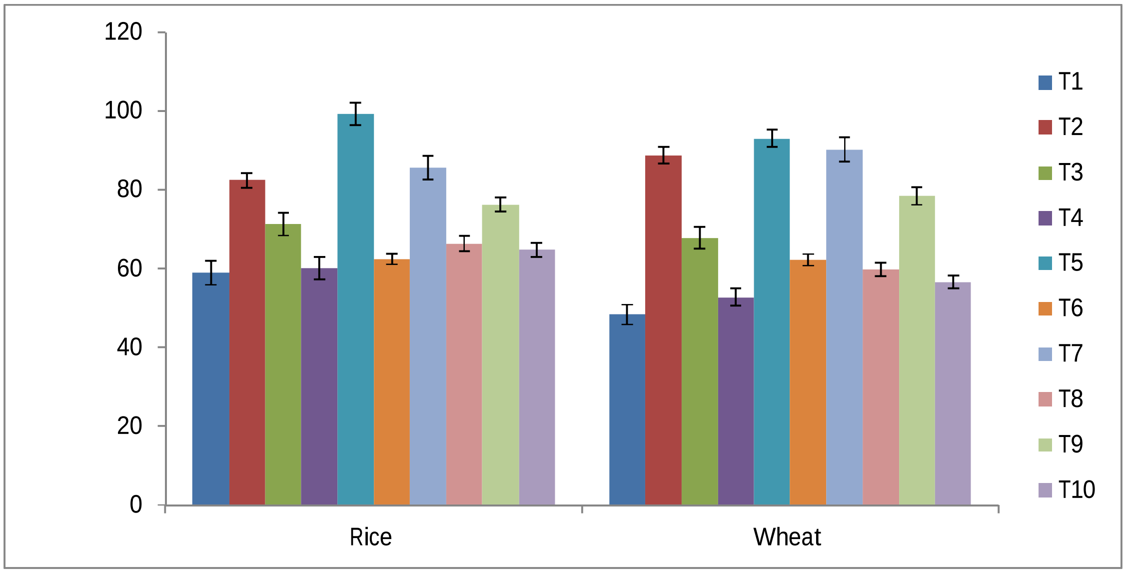


Figure 4.33 Effect of different fertilizer treatments on acid phosphatase activity in rice and wheat crops

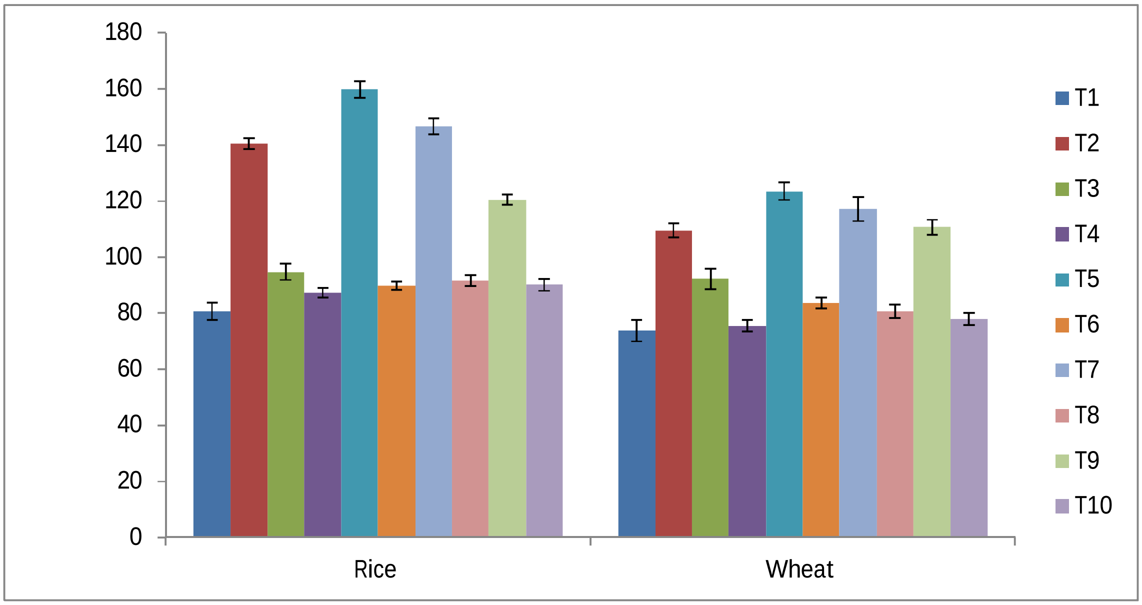


Figure 4.34 Effect of different fertilizer treatments on alkaline phosphatase activity in rice and wheat crops

low level. Increased emission from all the pots after urea application could be due to nitrification.

The ANOVA analysis revealed that average daily N_2O fluxes in the rice season not differed significantly amongst various treatments. N_2O fluxes on 3 DAT in rice crop season ranged from 9.51 to 10.5 N_2O-N g ha^{-1} day^{-1} and were significantly lower in AA+Am NCPC, followed by Na-Alg NCPC, WF NCPC and urea but without any significant differences. Thereafter in all the treatments N_2O fluxes declined sharply and on 26 DAT they ranged from 4.88 to 5.74 N_2O-N g $ha^{-1}day^{-1}$. Application of N fertilizer on 30 DAT increased NH_4^+-N content in soil due to hydrolysis of urea. Under optimum moisture conditions 2–3 days are required for hydrolysis of urea. On the 33 day N_2O fluxes increased in all the treatments, but the increase was more in conventional fertilizer treatment and Na-Alg NCPC and AA+Am NCPC showed significant difference from urea and WF NCPC. Thereafter fluxes in all the treatments declined sharply till 57th DAT and significant differences were found amongst the treatments and they ranged from 4.80 to 6.40 N_2O-N g ha^{-1} day^{-1}, higher flux was seen in urea and WF NCPC as compared to AA+Am and Na-Alg NCPC. One more peaks in N fluxes was recorded on 63rd DAT as fluxes increased significantly in all the treatments and significantly different from urea except WF NCPC.

Average N_2O fluxes of all the sampling dates in the rice crop season in various treatments ranged from 5.91 to 7.10 N_2O-N g ha^{-1} day^{-1} and followed the order: Urea> WF NCPC> Na-Alg NCPC>AA+Am NCPC (Table 4.21). Total N_2O emissions in the rice season ranged from 0.405 to 0.339 Kg N_2O-N ha^{-1} and were significantly the highest in Urea followed by WF NCPC, Na-Alg NCPC, and AA+Am NCPC. The highest N_2O emission was due to the application of 100% urea followed by WF NCPC and Na-Alg NCPC in which denitrification increased after the mineralization of polysaccharide and fast release of N. Lowest N_2O emission in the AA+Am NCPC treatment was probably due to lack of substrate for denitrifying bacteria because of slow release of N from it.

4.3.20.2 N_2O emissions in wheat

In wheat on day 3 emission of N_2O ranged from 6.90 to 8.08 g ha^{-1} day^{-1}, which reduced till the next dose of urea was applied (Figure 4.36). A peak was observed in all the treatments following the addition of urea and NCPCs which may be due to vigorous nitrification when sufficient NH_4^+- N was present in soil followed by a decline to reach a low level of N_2O emissions. Denitrification might also have taken place in some anaerobic microsites in the soil, resulting in N_2O-N flux. All the NCPCs used in this study were effectively reduced N_2O emission (Table 4.21) due to slow release behavior.

In the wheat crop season average N_2O fluxes in different treatments ranged from 3.33 to 8.08 N_2O-N g ha^{-1} day^{-1} during the 70 days of growing periods and were comparatively lower than rice season (Figure 4.36). The effect of various treatments on N_2O fluxes was significant and they decreased in following order: Urea> WF NCPC> Na-Alg NCPC>AA+Am NCPC. Total N_2O emissions in the wheat crop season in urea treated pots were 0.337 N_2O-N kg ha^{-1}, which were significantly higher than all the other treatments. Though total N_2O emission in other treatments varied from 0.295 to 0.310 N_2O-N kg ha^{-1}, but the differences were insignificant (Table 4.21). It was observed that average and cumulative N_2O fluxes in wheat season were lower than rice season, which were probably due to lower soil temperature.

The ANOVA analysis revealed that average daily N_2O fluxes in the wheat season differed significantly amongst various treatments on various gas sampling dates. In the wheat crop season, daily N_2O fluxes were comparatively lower than rice crop season and they ranged from 4.49 to 5.26 N_2O-N g ha^{-1} day-^{1} (Table 4.21) were not significantly different, and on subsequent days the fluxes remained in lower range till the first dose of fertilizer N was applied. N_2O flux at 11 DAS was significantly low in AA+AM NCPC while in all other treatments (urea, WF NCPC and Na-Alg NCPC) differences were insignificant. Thereafter in all the treatments N_2O fluxes declined sharply and on 18 DAS they ranged from 3.93 to 4.91 N_2O-N g $ha^{-1}day^{-1}$. Application of N fertilizer on 30 DAS increased NH_4^+-N content in soil due to hydrolysis of urea. Under optimum moisture conditions 2–3 days are required for hydrolysis of urea. On the 33 day N_2O fluxes increased significantly in all the treatments, but the increase was more in conventional fertilizer treatment. Thereafter fluxes in all the treatments declined sharply till 55th DAS and they ranged between 3.81 to 4.36 N_2O-N g $ha^{-1}day^{-1}$. One more peak in N fluxes was recorded on 63rd DAS as fluxes increased significantly in all the treatments and differences amongst the treatments was significant for urea only in comparison to Na-Alg and AA+Am

Table 4.22 Interrelationships between grain yield and soil chemical and biological properties in rice

	Total yield	Total N	Total N uptake	Total chl	Mineral N	SOC	TN	MBC	MBN	Urease	DHA	Acid P age	Alk P age
Total yield	1												
Total N	.781**	1											
TotalN uptake	.858**	.973**	1										
Total chl	.897**	.705*	.833**	1									
Mineral N	.791**	.825**	.924**	.894**	1								
SOC	.907**	.772**	.840**	.864**	.764*	1							
TN	.823**	.932**	.959**	.800**	.855**	.872**	1						
MBC	.868**	.790**	.894**	.958**	.924**	.829**	.870**	1					
MBN	.836**	.892**	.953**	.842**	.928**	.799**	.909**	.942**	1				
Urease	.810**	.706*	.841**	.958**	.957**	.766**	.789**	.940**	.853**	1			
DHA	.803**	.712*	.786**	.865**	.760*	.674*	.766**	.894**	.803**	.810**	1		
Acid page	.792**	0.613	.732*	.877**	.811**	0.605	0.628	.903**	.825**	.863**	.899**	1	
Alk page	.800**	0.607	.737*	.928**	.835**	.654*	.643*	.905**	.784**	.922**	.900**	.971**	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

NCPC treatments. While, difference between urea and WF NCPC was insignificant on 63rd day.

4.3.20.4 Soil parameter influencing N_2O emission

4.3.20.4.1 Carbon and Nitrogen

Plotting N_2O emission against soil organic C content gave a negative nonlinear relationship in both rice and wheat crops (Figure 4.37a and 4.38a), suggesting that agricultural soils with higher organic C yield lower N_2O emissions. Figure 4.37b and 4.38b shows the relationship between N_2O emission and soil total N content. This relationship is similar to that with soil organic carbon content, because N_2O emission decreased linearly with an increment in the soil N content.

Table 4.23 Interrelationships between grain yield and soil chemical and biological properties in wheat

	Total yield	Total N	Total N uptake	Total chl	Mineral N	SOC	TN	MBC	MBN	Urease	DHA	Acid P age	AlkP age
Total yield	1												
Total N	.865**	1											
TotalN uptake	.967**	.949**	1										
Total chl	.907**	.738*	.886**	1									
Mineral N	.960**	.805**	.906**	.913**	1								
SOC	.817**	.834**	.884**	.852**	.830**	1							
TN	.929**	.749*	.889**	.933**	.964**	.875**	1						
MBC	.905**	.765**	.883**	.897**	.936**	.892**	.934**	1					
MBN	.900**	.730*	.890**	.886**	.862**	.872**	.925**	.930**	1				
Urease	.809**	0.591	.730*	.830**	.915**	.725*	.928**	.834**	.759*	1			
DHA	.775**	.708*	.824**	.858**	.762*	.794**	.846**	.813**	.863**	.746*	1		
Acid page	.817**	0.632	.786**	.856**	.878**	.822**	.924**	.952**	.911**	.883**	.879**	1	
Alk page	.763*	0.59	.745*	.796**	.817**	.837**	.890**	.934**	.919**	.816**	.840**	.982**	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

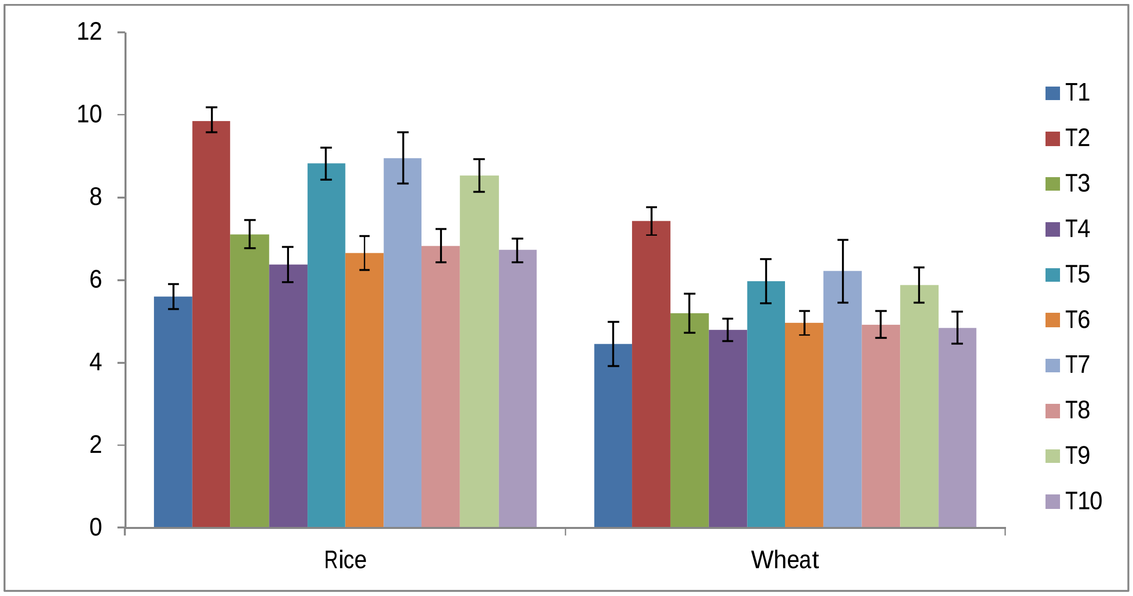


Figure 4.31 Effect of different fertilizer treatments on urease activity in rice and wheat crops

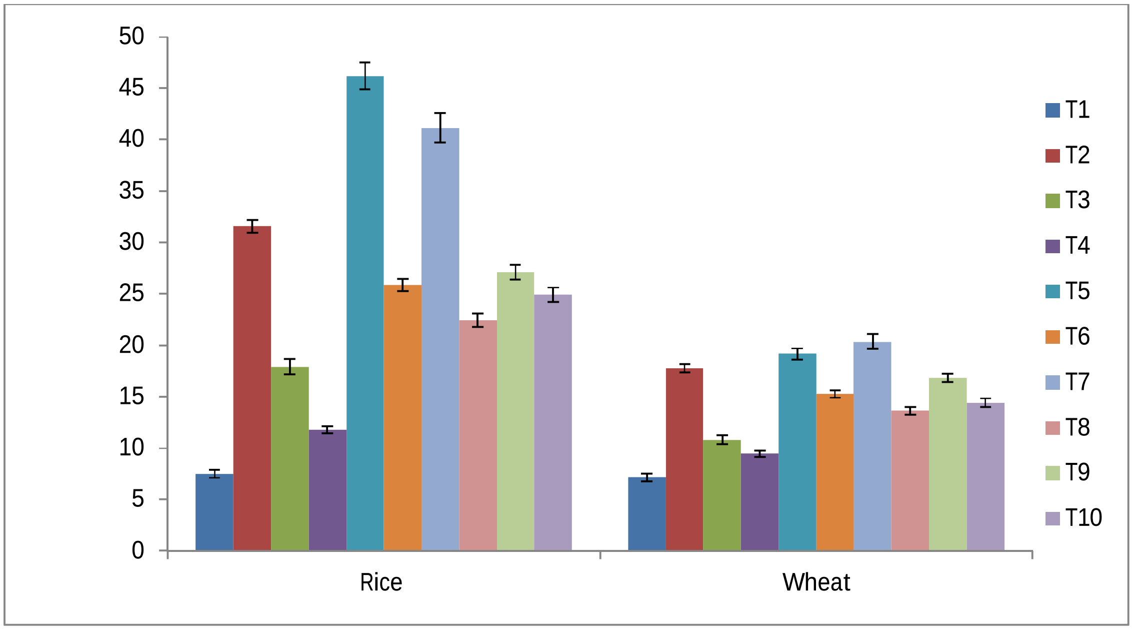


Figure 4.32 Effect of different fertilizer treatments on dehydrogenase activity in rice and wheat crops

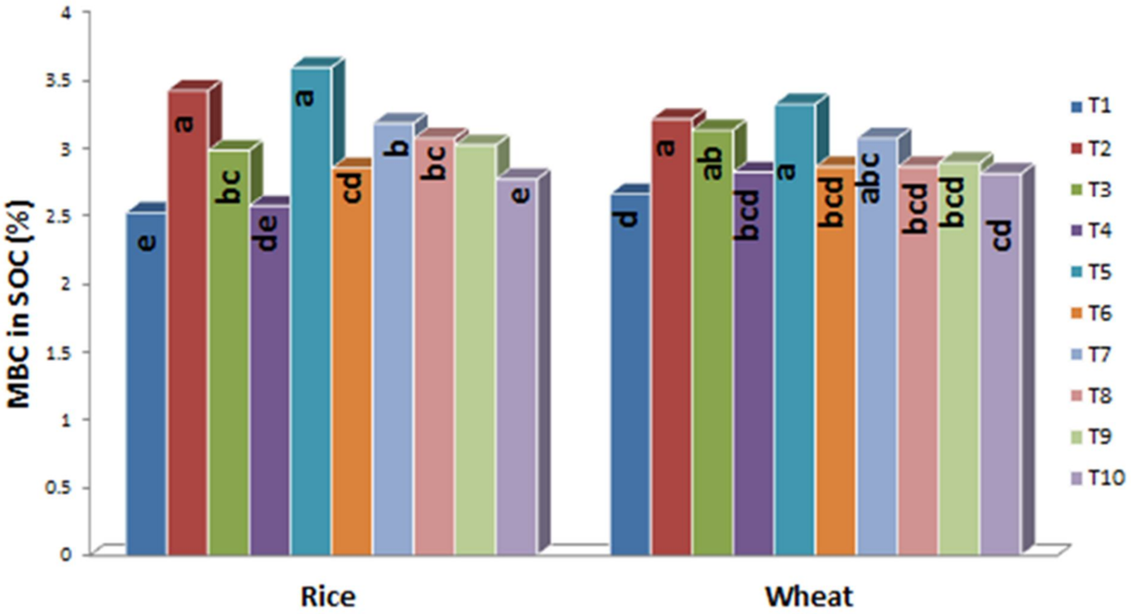


Figure 4.29 Percentage of MBC in SOC after harvesting of rice and wheat

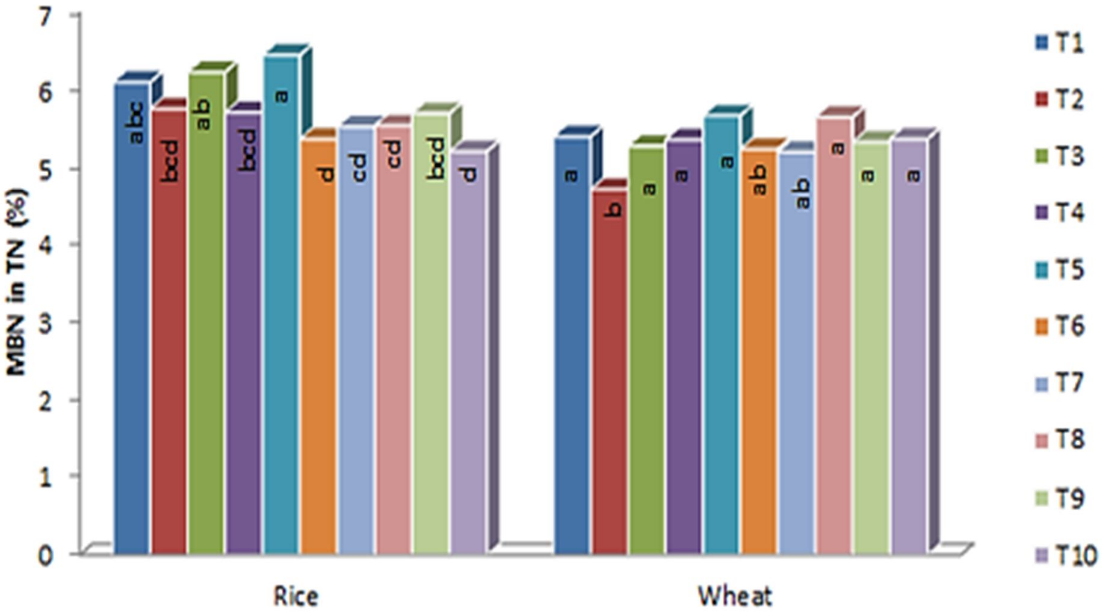


Figure 4.30 Percentage MBN in TN in rice and wheat soil after harvesting

Table 4.20 Effect of different fertilizer treatments on urease, dehydrogenase, and phosphatase activity in rice and wheat crops

Treatments	Urease (µg urea g^{-1} h^{-1})		Dehydrogenase (µg TPF g^{-1} h^{-1})		Acid phosphatase (µg PNP g^{-1} h^{-1})		Alkaline phosphatase (µg PNP g^{-1} h^{-1})	
	Rice	**Wheat**	**Rice**	**Wheat**	**Rice**	**Wheat**	**Rice**	**Wheat**
T1	5.60^{d}	4.45d	7.47^{h}	7.14^{g}	58.96^{f}	48.42^{f}	80.66^{f}	73.8^{e}
T2	8.82b	5.97b	31.56^{c}	17.76^{b}	82.45^{bc}	88.79^{a}	140.49^{b}	109.52^{b}
T3	7.11c	5.2^{c}	17.9^{f}	10.81^{e}	71.43^{d}	67.78^{c}	94.71^{e}	92.27^{c}
T4	6.37c	4.79^{cd}	11.78^{g}	9.45^{f}	60.12^{f}	52.77^{ef}	87.32^{ef}	75.6^{de}
T5	9.84a	7.43^{a}	46.19^{a}	19.15^{a}	99.31^{a}	93.09^{a}	159.81^{a}	123.49^{a}
T6	6.65c	4.96^{cd}	25.86^{d}	15.25^{c}	62.49^{f}	62.31^{cd}	89.76^{ef}	83.74^{c}
T7	8.96b	6.21^{b}	41.15^{b}	20.37^{a}	85.66^{b}	90.23^{a}	146.65^{b}	117.1^{ab}
T8	6.83c	4.92^{cd}	22.43e	13.65^{d}	66.32^{e}	59.86^{d}	91.63^{ef}	80.62^{de}
T9	8.53b	5.88^{b}	27.12d	16.84$_{b}$	76.29^{d}	78.44^{b}	120.5^{c}	110.65^{b}
T10	6.72c	4.85^{cd}	24.91d	14.44^{cd}	64.78^{ef}	56.59^{de}	90.34^{ef}	77.9^{de}

Means are the average of three replicates. Means followed by a common letter are not significantly different at the 5% level based on Duncan’s Multiple Range Test (DMRT).

5.1.1 Infrared spectroscopy (FTIR)

FTIR is a powerful technique for investigating intermolecular interactions of certain functional groups. Therefore, in the case of hydrogels, the formation of hydrogen bonds in a randomcopolymer hydrogel such as poly (acrylic acid–co–acrylamide) will influence these molecular interactions. The FTIR spectra showed that the absorption bands of –OH stretching of clay in the range 912, and 3619 cm^{-1} disappeared, and the absorption bands at about 1032 cm^{-1}, ascribed to the Si-O stretching of clays, were weakened after the incorporation of clay into the polymer network. It was suggested that graft copolymerization between the -OH groups on kaolin and the monomers took place during the polymerization reaction (Liang & Liu, 2007). Lin *et al*. (2001) reported that AA could graft onto mica and form a poly (acrylic acid)/mica superabsorbent composite. The -OH group of kaolinite could react with acrylamide, and kaolinite particles could chemically bond with the polymer chains to form a starch-graft-acryl amide/kaolinite composite (Al-Zahrani, 2000).Thus, the disappeared and weakened absorption bands mayhave been due to the same reason, and the clays reacted with monomer unit during the polymerization process. The FTIR spectrum of the NaAlg–g–p(AA–co–AAm)/Clin/NPK fertilizer showed the corresponding peaks of NPK fertilizer. In ahigher frequency region, a main band at 3432 cm^{-1} with two shoulders at 3585 cm^{-1} and 3232 cm^{-1} are assigned to the two asymmetric stretching and symmetric stretching modes of the NH_2 groups in urea. Also a sharp peak at 1615 cm^{-1} is assigned to the C=O stretching mode related to urea (Rashidzadeh *et al.*, 2014).

Shi *et al.*, (2012) prepared alginate-based superabsorbentand found composite with grafted copolymerization partially neutralized acrylic acid (NaA), styrene (St) onto the sodium alginate (NaAlg) backbones in the presence of attapulgite (APT) [NaAlg-g-poly(NaA-co-St)/APT]. They found that the characteristic absorption bands of NaAlg at 1098 and 1031 cm^{-1} (stretching vibration of C-OH groups) were weakened after reaction, which indicate the -OH groups of NaAlg participated in chemical reaction. The hydrated surface (Si) O-H stretching vibration of APT at 3545 cm^{-1} disappears and the intensities of Si–O absorption band at 1031 cm^{-1}

weakened, confirming that APT participated in the grafting copolymerization reaction by its active silanol groups.

Jin *et al.*, (2013) found the characteristic peaksfor the saccharide structure of starch in starch/poly(acrylic acid-co-acrylamide) superabsorbent, at 1649.11 and 1159.07–992.53 cm^{-1}, which could be assigned to symmetric and asymmetric stretching vibrations of the C-O-C bridge, respectively. It was evident that a stronger and wider peak appearing at about 1658.70 cm^{-1}, was due to the symmetric stretching vibration of the C-O-C bridge, which wasoverlaid with the stretching vibration of C=O (amide I). At the same time, the multiplet observed at about 1117.44 cm^{-1} may have corresponded to the asymmetric stretching vibration of the C-O-C group of carbon 6. Thisfact, together with the new peak appearing at 1293.62 cm^{-1}, corresponded to its symmetric stretching vibration and implied a successful O-site grafting polymerization reaction.

5.1.2 X-ray diffraction analysis

The crystalline peak of montmorillonite (MMT) observed at about 7.33 corresponds to the periodicity in the direction of (001) of the MMT (Wang *et al.*, 2003). In the case of Hydrogel/MMT/NPK, the diffraction peak related to montmorillonite is disappeared which is an indicativeof exfoliated structure. In exfoliated structures no more diffraction peaks are visible in the XRD diffractograms either because of a too large spacing between the layers or because the nanocompositedoes not present ordering. The extensive layer separationassociated with exfoliated structures disrupts the coherent layerstacking and results in a featureless diffraction pattern (Pavlidou & Papaspyrides, 2008). The XRD pattern of AA+Am NCPC, WF NCPC and Na-Alg NCPC did not show the characteristicbasal peak of bentonite particles after their incorporation into the polymer matrix. This indicates that the silicate layers of bentonite were completely exfoliated in final product after polymerization process. According to Leitão *et al.*, (2015), clay particles dispersed in the nanocomposite matrix due the formation of H-bonds between the amide and acid groups present on the polymer matrix and water molecules surrounding the exchangeable cations on clay particles. The exfoliated nature of the nanoclay was due to the long polymer chains of the polymer matrix that were inserted into the gallery space of the nanoclay, leading to an increase in the interlayer spacing of the silicate layers. The extensive layer separation associated with exfoliated structures disrupts the coherent layer stacking and results in a featureless diffraction pattern. Thus, the reason for the no diffraction peaks of exfoliated structures in XRD diffractograms are either because of a very large spacing between the layers (i.e. exceeding 8 nm in the case of an ordered exfoliated structure) or because the nanocomposite does not present ordering (Pavlidou & Papaspyrides, 2008; Vaia and Giannelis, 1997). Peaks observed for sodium alginate powder at 13.5, 21.8, and 38.6 degree 2θ may be assigned to the reflection of their (1 1 0) plane from the polyguluronate unit, (2 0 0) plane from the polymannuronate, and others from amorphous halo (Beherei *et al.*, 2011). Fang *et al.* (2011) suggested crystalline nature of the sodium alginate powder mainly due to strong intermolecular hydrogen bonding between alginate chains.

5.1.3 Transmission electron microscopy (TEM)

The TEM micrographs revealed that size of the particles in the commercial bentonite was less than 100 nm. TEM observations of the images showed the flaky and plate-like bentonite clay particles with pseudo–hexagonal morphology (Al-Qunaibit M. and Al Juhaiman, 2012). These bentonite particles were found embedded in the polymer matrices. This result is in conformity with the results of Wang & Wang, 2010. In another study, Amin *et al.*, 2013 reported the same thing, where they observed stacks of the intercalated clay platelets (montmorillonite) embedded in the vinyl polymer matrices, showing good distribution of the montmorillonite particles within the polymer matrices.

5.1.4 Scanning electron microscopy (SEM)

Bunnak *et al.*, (2014) & Masindi *et al.*, (2015) described bentonite clay as leafy, lamella like structures with several pores and reported that bentonite possesses plate like structure in the SEM image (Figure 4a). Rashidzadeh & Olad, (2014), found higher absorption of water by NaAlg-g-poly(AA-co-Am)/ montmorillonite encapsulated NPK fertilizer, as montmorillonite act as the physical crosslinking agent, therefore homogeneity as well as the pore size structure of the copolymer decreases, but the number of pores and channels increases and, consequently, the hydrogel with clay was expected to swell more. Liang and Liu (2007) observed that cross-linked AA/AM/kaolin-urea displayed the coarse surface, which could facilitate the more absorption of water into the polymeric network, but decreased water absorbency trend was observed with increasing kaolin content. The reasons for the decreasing of water absorbency with the increase of clay content was given by them as follows: firstly, the introduction of bentonite particles into the polymer increased the crosslinking density of poly(AA-co-Am)/ kaolin composite, which resulted in a decrease in water absorbency; secondly, the physically filling of clay particle in the polymer decreases the amount of hydrophilic groups, and consequently resulted in the reduction of water absorbency.

5.1.5 Scanning electron microscopy energy dispersive X-ray (SEM-EDX)

The SEM-EDX analysis confirmed the composition of the prepared NCPCs that regions in the SEM images correspond to urea crystals redispersed, because the elements detected were predominantly N, C and O, that is, urea constituents. On the other hand, the regions correspond to urea-intercalated bentonite, because significant amounts of Si and Al (clay constituents) and smaller N amounts were detected. The EDX spectra of the poly(acrylamide-*co*-acrylate) matrix filled with nontronite (NONT) was observed by Leitão *et al.*, (2015) and found peaks accounting to the elements C, O, and K. Whereas, the EDX spectrum of PAMACRYL/NONT10 showed the characteristic peaks assigned to the elements Si and Al. All of them confirmed the successfully formation of the superabsorbent nanocomposite.

5.1.6 Water absorption and swelling kinetics in water by NCPCs

Dense polymeric network and more number of large pores in AA+Am and Na-Alg NCPC resulted in more water absorption by them as compared to WF NCPC. Whereas, smaller three-dimensional net hole due to the rather compact structure of the NCPC with 50 wt % starch resulted in less water absorption (Jin *et al.*, 2013). Rashidzadeh *et al.*, (2014) reported that due to negative surface charge of the clay, high repulsive forces between –COO^- groups of polymer and negative surface charge of bentonite increased expansion of the hydrogel network and a higher swelling ratio. Rashidzadeh *et al.*, (2014) also observed that, when clinoptilolite content was higher than 10%, a further increase in the crosslinking density of the hydrogel network would decrease the space among the grids of the hydrogel network. This would make it more difficult for the network to be swollen by water, which was responsible for the decrease in water absorbency.

According to previous studies (Sarkar *et al.,* 2014, Zhang *et al.*, 2007 and Li & Wang, 2005) and in this investigation, clay plays an important role in influencing properties of superabsorbent clay- polymer nanocomposite, since it is the reaction between clay (–OH on the clay surface) and monomers that form superabsorbent composite polymeric network results in increased water absorption. According to Flory's theory (1953), the water absorbency of a gel is dependent on ionic osmotic pressure, crosslinking density and the affinity of the gel for water. Buchanan *et al.* (1986) suggested that the swelling kinetic for the absorbent is significantly influenced by swelling capacity, specific surface area, and apparent density of the polymer. Higher clay concentration in polymer increased crosslinking and lesser water absorption. This was in conformity with the finding of some previous studies (Zhanget al., 2007; Liang and Liu, 2007). The results revealed that the swelling behaviour of the absorbent polymer depends on the composition of the polymer and the characteristics of the external solution. The swelling of hydrogels containing urea decreased with increased concentration of ammonium nitrate. The reason is the presence of ionic groups during agrochemicals' release in water. These ions prevent water molecules from diffusion into the hydrogels, thus decreasing the swelling capacity of the hydrogels. This result was in conformity with previous study of He *et al.* (2007).

5.1.7 Slow release behaviour of NCPCs in soil

The fertilizer release mechanism of prepared NCPCs in soil could be illustrated as followings: the fertilizer formulation was loaded with urea solution and dried, which can easily dissolve in water, and therefore the fertilizer is released out to the medium. At first, after being added into soil, NCPC would be slowly swollen by the water in soil and transformed to hydrogel. Then the fertilizer entrapped into polymeric network or on its surface could be slowly dissolved. In the next stage, the fertilizer would slowly be released into the soil through the superabsorbent nanocomposite with the dynamic exchange of the water in the hydrogel and the water in the soil. In this stage, diffusion would be the release rate-limiting step. With the increase of swelling ratio of superabsorbent nanocomposite, the aperture size of the three-dimensional network of NCPC increases which benefits the diffusion of the fertilizer into the soil. This phenomenon continues until the equilibrium swelling ratio ofsuperabsorbent nanocomposite. After that the fertilizer release into the soil decreases and becomes constant.

Jin *et al.*, (2013) reported in their study that starch superabsorbent fertilizers showed the similar trend of curve for both water absorption and nutrient release i.e. higher the water absorption, higher was the release rate. The reason they explained behind such phenomena is that the apertures in the three-dimensional network of the swollen hydrogel were bigger with higher WAs. As a result, the exchange of free water between the solution and the network and the nutrient released through it was easier. But, in this study in case of WF NCPC we got less water absorption and higher nutrient release. This might be because of larger number of small three-dimensional net hole which make them compact at 50 wt% starch as observed in SEM micrograph, so the water absorption was less. Less swelling of WF NCPC resulted in less absorption of urea inside the hydrogel network and more adsorption on the surface of NCPC. The other possible reason for more N release from WF and Na-Alg NCPC as compared to AA+Am NCPC was due to degradation of these NCPCs. During the period of degradation study it was found that starch and alginate NCPCs lost weight faster than the AA+Am NCPC (Figure 4.18).

5.2 Evidences of biodegradability

5.2.1 CO_2evolution measurements

Mineralization occurs when the polymer chains are metabolized by microorganisms after the initial chain scission process to carbondioxide (CO_2), water, and biomass (Moore & Saunders, 1998; Premraj & Doble, 2005). Hence, the degree of aerobic biodegradation can be determined by measuring the CO_2 evolved as a function of time that the polymers were exposed to soil (Modelli *et al.*, 1999; Calmon *et al.*, 2000). In this study we found increased evolution of CO_2 in WF and Na-Alg NCPC treated soil as compared to AA+Am NCPC, this might be due to presence of more labile C in WF and Na-Alg. Baldrian *et al.*, (2011) reported that biopolymers are highly biodegradable and represent a source of C for saprophytic fungi. Therefore, applying a biopolymer may result in an increase in soil microorganism and enzyme activities followed by an increase C mineralization which results in higher CO_2 efflux.This is in line with the previous observations that the incorporation of biodegradable materials increases the biodegradability.

5.2.2 Weight loss of NCPCs

In this study, the degradation of WF, Na-Alg and AA+Am NCPCs were monitored by the examination of the weight loss of the polymer with incubation time in soil at ambient temperature. Kelner and Schacht (2005) reported that the type of degradable link and the structure ofthe network play important roles in the control of the degradation behavior. Jin *et al.* (2013) reported that in starch/poly(AA-co-AM) hydrogel network four linkages are present glycosidic bonds of the starch molecules, amide links(-CO-NH-) from the crosslinker, ether links (-O-) of grafted poly(AA-co-AM), and alkyl linkages formed via radicalcopolymerization. And degradation of the superabsorbent depends on the breakage of glycosidic bonds, amide links, and ether bonds.The starch was invaded by bacteria, fungi, and other microorganisms under the appropriate temperature and moderate conditions when superabsorbent was incubated in soil. Simultaneously, amide links and ether links were broken through hydrolysis. Finally, these actions were sufficient to degrade the polymer into carbon dioxide and water.

During the incubation period we investigated that the NCPC with 50 wt % starch lost weight faster than Na-Alg and AA+Am NCPC. The rate of weight loss of AA+Am NCPC was the slowest. Result indicated that WF NCPC was partially degraded and could be used as NCPC fertilizers to lessen the environmental pollution. Similar result was obtained by Ni *et al.* (2010) where they used slow release coated fertilizer made up of sodium alginate as an inner coating and sodium alginate-g-poly(acrylic acid-co-acrylamide)/humic acid as an outer coating. Interpenetrating polymer network was synthesized by Kaith *et al.* (2016) using natural polysaccharide backbone with acrylic acid and acrylamide and is found to be highly biodegradable (completely degraded within 70 days using composting method, while it was 86.03% degraded within 77 days using soil burial method) leaving behind CO_2, H_2O and humus without any adverse impact on the fertility of the soil. This happened because of the presence of active species of different microorganism in the compost as well as in soil which accelerate the process of degradation (Albertsson *et al.*, 1987; Kaith *et al.*, 2010). Thus synthesized biodegradable superabsorbent fertilizer is very important in agriculture point of view (Wang & Wang, 2010; Montesano *et al.*, 2015). Unlike the high weight loss of biopolymeric superabsorbent as observed by Kaith *et al.* (2016), we found only 32.8% and 23.12% of weight loss in WF and Na-Alg NCPC after 90 days of incubation, because in our study degradation study of polymers was not done with direct contact of soil but in muslin cloth. Further, we have incorporated 10 wt % of bentonite clay in NCPCs. Similar observation was reported by Lee *et al.* (2002) on the biodegradation of aliphatic polyester-based nanocomposites in compost. They claimed that the biodegradation was slow due to improvement of the barrier properties after nanocomposite preparation with clay, which restricted the penetration of microorganism through the material. Generally, barrier properties of polymer nanocomposites are highly dependent on the dispersion and distribution of clay platelets in the polymer matrix (Frounchi *et al.*, 2006).

5.2.3 FTIR Spectra

Biodegradation of NCPCs brought some structural changes in the FTIR spectra of the polymers. There were several peaks which were present earlier absent in the sample after biodegradation. And there were different new peaks also found after degradation. In case of WF NCPC bands related to O-H stretching and C-O from glycosidic bond disappeared after degradation because of easily degradable nature of polysaccharides. Mittal *et al.* (2010) observed shifting of peaks at 1731, 2928, 1456 and 1166 cm^{-1} after degradation in polyacrylamide polymers due to starting of breaking down of the crosslinked network. Nnamonu *et al.* (2012) reported disappearance of 3000-3429 cm^{-1} band which corresponds to O-H stretching in sodium alginate polymer after degradation as natural polysaccharide (Na-Alg) is easily degradable. Ali *et al.* (2009) found that the FTIR analysis ofCellulose blended PVC film showed that the peak atwavelength 3245 cm^{-1} was present in control, which wasabsent in the sample after degradation. Okaya & Ikari (1992) observed the FTIR spectra of poly (vinyl alcohol) which showed a sharp decrease in the bands and peaks of the polymer after degradation.

5.3.1 Growth parameters

The taller plants were recorded for the treatments receiving urea @ 100% N of RDF. However, shorter rice plants were observed in other treatments due to the effect of lower rates of N fertilizers @ 75% and 50% N of RDF (Table 4.4). When fertilizer was applied @ 75% N of RDFthrough NCPCs plant height was also increased, and remained significantly at par with urea @ 100% rate. The greatest height among the NCPC (@ 75%) treated plant was found in T5 (WF NCPC), possibly due to more release of N than Na-Alg and AA+AM NCPCs duringthis period. Increased plant height in NCPC treatments as compared to conventional fertilizer, at same level of nitrogen (75% and 50% of RDF) might be due to synchronized N release and plant N demand.The increase in plant height in response to application of N fertilizers is probably due to enhanced availability of adequate nitrogen and assimilates, which enhance plant growth (Indira, 2005; Chaturvedi, 2005). Irshad *et al.* (2000) reported that plant height significantly increased by nitrogen application. Salman*et al.* (2012) reported that plant height showed significant effect with nitrogen treatment.The results of this study also corroborate the findings of Hussain and Shah (2002), and Pervez *et al.* (2009) who reported that the height of wheat plants increased with the increase in the application rates of nitrogen fertilizer.

The higher panicle length was obtained in rice and wheat with the application of urea @ 100% N of RDF across application times. However, application of lower dose of fertilizer @ 75% N of RDF) as NCPC was equally effective with higher dose of conventional fertilizer in terms of increased panicle/spike length. Reducing N @ 50% of RDF, significantly lowered panicle length in all fertilizer treatments. Metwally *et al.* (2011) also found significantly greater panicle length due to the role of nitrogen in crop maturation, flowering and seed formation. Spike length became higher at higher dose of N possibly due to higher availability of nitrogen (Hameed *et al.*, 2002). This result was also in agreement with that of Laghari *et al.* (2010) who reported that spike length of wheat crop became higher at the higher doses of nitrogen.In contrast to our results, Abd El-Maksoud (2008) found non-significant results for rice panicle length under the effect of N fertilizers applied.

5.3.2 Yield components

5.3.2.1 Straw and grain yield

The maximum straw yield was found from 100% N of RDF supplied through conventional fertilizer and remained significantly equal with the NCPCs applied @ 75% N of RDF. All the treatments applied with NCPCs (@ 75%) yielded higher straw weight in rice and wheat due to long last release of N from these treatments (Lyu *et al.*, 2015). The significant increase in straw yields of rice and wheat in response to increasing the rate of N fertilizer may be attributed to increased plant height and tillering. Straw yield is reflected by growth parameters like total number of plants, tillers per unit area and final plant height. Nitrogen application enhances the vegetative growth of wheat crop and delays senescence, which ultimately increases biological yield (Samad *et al.*, 2005). Consistent with the results of this study, Allam (2003), Iqbal *et al.* (2012) and Khurram *et al.* (2013) reported increases in straw yield with added nitrogen to soil.

The increase in grain yield in response to increasing the nitrogen rate could be attributed to enhanced availability of the nutrient for uptake by the plants and increased photo assimilate production that would eventually lead to improved partitioning of carbohydrate to the grains (Gooding and Davies, 1997). The increased availability of nutrients on addition of fertilizer as NCPC was found equally effective with higher dose of conventional form in terms of grain yield. The possible reason in yield enhancement by these might be due to continuous and steady supplyof N into the soil by NCPC fertilizers to meet the required nutrients for physiological processes, which in turn improves grain yield. Similar findings were reported by Maynard and Lorenz, (1979), where they suggested that higher grain yield by wheat and rice under controlled release fertilizer maintained the nutrients in soil for an extended period.

5.3.3 Nitrogen concentration and uptake

Nitrogen content in straw and grain were affected significantly with the application of various nitrogen fertilizers compared with control (T_1). Nitrogen content in straw and grain increased with increase in fertilizer N level; however the differences between the treatments were statistically at par. Guarda *et al*. (2004) reported that the rise in yield and the enhanced N-use found to be coupled to diminished grain N% linked to a dilution effect in the amount of nitrogen (protein) due to increase in the amount of carbohydrates (Kibite and Evans, 1984). Uptake increased significantly with increase in N level, while the lowest uptake of N was recorded in control. The lower uptake in control is due to the lower yield obtained in these pots. Our findings showed that increase in straw and grain N-accumulation in NCPC treatments matched by yield increments. Consequent upon higher yield of grain and straw in T_5, T_7 and T_9 the uptake of N was also significantly higher in these treatments and was equally effective with higher dose of conventional fertilizer in terms of nitrogen uptake. Since nutrient uptake is the product of nutrient concentration and yield, hence, uptake generally followed the yield trend. The increase in uptake in N may be due to better availability and absorption of N in balanced quantity because of good proliferation of root system (Sharma *et al.,* 2001). Nutrient uptake is an important process, which decides all improvement in plant growth, yield and quality of crop produces. When controlled release fertilizers (CRFs) are applied the chemical properties of the soil are improved as compared to commercial fertilizers (Mikkeison *et al.* 1994) and the utilization of nutrients by plants at critical stages are also increased as in CRF the release of nutrients is for an extended period (Maynard and Lorenz 1979). Sarkar & Datta, 2014 reported higher uptake of P and N than conventional fertilizer, treatment NCPC-H (higher dose) resulted in 17.0% and 11.0% additional uptake of P and N, respectively, over the CF-H (conventional fertilizer at higher dose), while treatment NCPC-L (lower dose) resulted in 23.0% and 16.0% higher uptake of P and N, respectively, over the CF-L (conventional fertilizer at lower dose). They suggested that the use of CRF might have allowed the nutrients to be used more efficiently by plants than soluble conventional N fertilizers by reducing N leaching and other losses and providing a constant supply of nutrients to the roots (Mikkelson *et al.*, 1994). Moreover, superabsorbent polymer acts as a micro-reservoir to retain and supply nutrients to crops along with moisture, and thus could increase the utilization efficiency of nutrients and water at the same time (Liang *et al.*, 2007). All the reasons specified above might have enhanced the uptake of N by wheat and rice when fertilizer loaded NCPC was applied to the soils.

5.3.4 Nitrogen use efficiency

NCPCs are capable to store large quantities of water and nutrients and released slowly as required by the plant to improve. The highest values of nitrogen use efficiencies with NCPCs were may be due to the regulated release of nitrogen. The significant increase in N uptake in response to the combined application of urea and polymer composites could be attributed to increased nutrient, soil moisture availability, the soil physio-chemical properties and enhanced fertilizer use efficiency resulting in greater nutrient uptake by plant roots.Nitrogen use efficiency and nitrogen agronomic efficiency (NAE) are major indicators of N efficiency in the field (Moll *et al.*, 1982). In general, 20–40% of NUE and 10–20 kg grain kg^{-1} N of NAE could be improved by the decrease of N supplement to rice (Cassman *et al.*, 2002; Zhuand Chen, 2002; Wang *et al.*, 2007). Results of this study indicated that NCPC application had significantly higher aboveground biomass (yield plus straw), ARE, AE and PE compared to conventional fertilizer. These advantages of NCPC over urea might be due to the synchronized release of N. Application of NCPC increased the residual N in the soil compared to urea, particularly in late crop growth period, resulting in higher N uptake in rice and wheat (Table 4.7). As a consequence, NUE was increased and N losses was decreased under NCPC. Similar findings were reported by Xu *et al.* (2013).

Green *et al.*(2004) found polyacrylamide as an effective soil conditioner for enhancing the stability of soil aggregates and increase soil infiltration in some areas especially in sandy loam soils (Green *et al.*, 2000). Polyacrylamide (PAM) is a long-chain synthetic polymer that acts as a strengthening agent, binding soil particle together and holding soils in place, but Polyacrylamide alone not remediate poor soil structure (Cook *et al.*, 1986). Maghchiche *et al.* (2010) found among synthetic polyacrylamide and blend of polyacrylamide-cellulose, latter one performed well in improving soil physical properties and water retention. Sojka *et al.*(2007, 2005) reported that using biopolymers (BPs) produced from starch, cellulose, chitin, lignin, microfibril suspensions, polysaccharides and protein derivatives are an eco-friendly alternative to polyacrylamide to prevent soil erosion. Biopolymers stabilize soil aggregates through their surface charge and retain their stability in aqueous suspensions (Orts *et al.*, 2000). In particular, cellulose microfibrils in BPs (crystalline units of cellulose) are dispersed in water during acid hydrolysis through the charge on their outer surface, thereby resulting inclay flocculation and stabilization of aggregates (Orts *et al.*, 2000). In contrast to PAM, BPs are highly biodegradable and represent a source of C for saprophytic fungi (Baldrian *et al.*, 2011). Therefore, applying a BP may result in an increase in soil microorganism and enzyme activities followed by stimulation of nitrogen (N) fixation as well as phosphorous solubilization (Saha *et al.*, 1995), leading to increment of available plant nutrients (Saenjan, 1999) in soil. Therefore, efficiency was higher in NCPC treatments.

Recovery efficiency and physiological efficiency (PE) were greater in wheat than in rice in this study. Cassman *et al.* (1993), on the other hand, found nearly identical PE for irrigated wheat in California and for dry-season irrigated rice in the Philippines. Adhikari *et al.* (1999) found in their study that solar radiation was higher and the temperature was cooler during the wheat season compared to the monsoonal rice season. Wheat season conditions therefore were conducive to a long and favorable grain development period (Spiertz, 1977), thus PE was greater in wheat than in rice. High temperatures exacerbate volatile losses of N during grain fill in both rice (Stutte and da Silva, 1981) and in wheat (Papakosta and Gagianas, 1990), which also helps explain higher PE in the cooler wheat season compared to rice. Higher RE of wheat compared to rice receiving the same N rate in the same field has been reported by Bronson *et al.* (1997) in Northwest India. They speculated that nitrification denitrification and leaching losses of fertilizer N were greater in rice than in wheat. In our study we also found higher N_2O emission and lower soil remaining mineral N in rice crop, resulted in lower efficiency than wheat.

5.3.5 Micronutrient content in grain

In this study, the concentrations of the microelements in wheat and rice increased with increasing N fertilizer application from 50 to 100% of RDF. Hao *et al.*, (2007) found that the Fe, Mn, Cu and Zn concentrations in brown rice of the two varieties (IR68144 and IR 64) reached the highest at 160 kg N/ha. Otherworkers have also found the similar findings (Brohi *et al.*, 1998, Pando *et al.*, 1985). However, in this study we found delayed biomass production in NCPCs treated pots due to slow release of nitrogen but plant growth and mineral accumulation (N, Fe, Zn, Cu and Mn) and their partitioning to grain (only nitrogen) did not differ significantly between plants fertilized with higher dose of urea. Similar findings were reported by Rose (2016).

5.3.6 Chlorophyll concentrations in leaves

Leaf chlorophyll concentration is often well correlated with plant metabolic activity (e.g., photosynthetic capacity and RuBP carboxylase activity; Evans, 1983; Seeman *et al.*, 1987), plant stress (Eagles *et al.*, 1983; Fanizza *et al.*, 1991), as well as leaf N concentration. Chlorophyll a content is an important parameter directly related to the amount of photosynthesis inthe plants and hence in turn to the final production. In our investigation it was observed that the total chlorophyll content was found higher in fertilized plants in comparison to the untreated control plants. Application of nitrogen directly increased the chlorophyll content and leaf surface area resulting in increased photosynthesis process leading to more sugar formation (Dikshit and Paliwal, 1989). Nitrogen nutrition influences the content of photosynthetic pigments, the synthesis of the enzymes taking part in the carbon reduction, the formation of the membrane system of chloroplasts, etc. Thus the increase in growth and yield owing to the application of N-fertilizers may be attributed to the fact that these nutrients being important constituents of nucleotides, proteins, chlorophyll and enzymes, involve in various metabolic processes which have direct impact on vegetative and reproductive phases of plants (Mengel and Kirkby, 1996). Verma *et al.*, (2004) recorded that the N content in the third leaf, chlorophyll a content increased with increasing nitrogen rate.

5.3.7 Availability of mineral N

Ammonium N content under conventional fertilizer (T_2) remained higher initially as compared to NCPC treated soil then started to decrease. This might be due to the fact that we have taken higher dose of N in T_2 as compared to other treatments. Whereas, at same level of N fertilizer, ammonium N content was significantly higher under NCPC treatments compared to conventional fertilizer. Higher amount of mineral N in conventional fertilizer treatments (T_2, T_3 and T_4) was observed than NCPC treated soil just after the fertilizer application (at 3, 33 and 63 DAS/DAT in rice and wheat). Further, rapid hydrolysis of urea under conventional fertilizer and subsequent nitrification resulted higher nitrate N content in soil in conventional fertilizer than NCPC treated soil. This indicated that NCPC could maintain a gradual release of loaded nutrients in soil for longer period. Among 3 NCPCs, AA+Am NCPC showed more soil mineral N availability throughout the growing crop growing period and higher N recovery efficiency (56.54% in rice and 68.52% in wheat), indicating its potential in the rice-wheat rotation system for increasing nitrogen use efficiency and decreasing nitrogen loss. In case of WF NCPC, higher soil remaining N after fertilizer application was observed also the recovery efficiency was less because of fast release of N because of compact structure at 50 wt% starch as observed in SEM micrograph, so the water absorption was less. Less swelling of WF NCPC resulted in less absorption of urea inside the hydrogel network and more adsorption on the surface of NCPC. The other possible reason for more N release from WF and Na-Alg NCPC as compared to AA+Am NCPC was due to degradation of these NCPCs. During the period of degradation study it was found that starch and alginate NCPCs lost weight faster than the AA+Am NCPC (Figure 4.18). Almost all the treatments were accompanied by a general decrease in total mineral N at harvest.

Sahrawat (1980) stated that when the soil samples contain relatively higher amounts of NH_4^+ it may be useful to employ the nitrification rates of soils with or without a nitrification inhibitors as the criterion for comparing the effectiveness of the compounds. Therefore, in this present study overall nitrification rates in different fertilizers treated pots were calculated in rice and wheat crop. The higher value of nitrification rate was observed in conventional fertilizer treatments than NCPC treatments, both in rice and wheat soil. Because in case of urea initially fast release of NH_4^+ -N just after the fertilization occurred which was subsequently converted to NO_3^- -N, whereas slow release NCPC fertilizers were able to maintain uniform amount of NH_4^+ -N throughout the crop growing periods.

5.3.8 Partial nitrogen balance in rice and wheat crops

Nitrogen depletes from rice field under frequent wet and dry irrigation. The higher unaccounted mineral N in conventional fertilizer treatments compared to NCPC treatments could be related to low plant uptake (Table 4.7) and low soil mineral N availability (Table 4.13 and 4.16) and higher N losses through various pathways (N_2O emission shown in Figure 4.35 and 4.36). The higher N uptake under slow release NCPC treatments could be due to synchronized N release from fertilizer and N requirement by the plant, which led to increased aboveground biomass accumulation. The present finding is in consistent with the findings of Shoji and Kanno (1994) and Xu *et al.* (2006). Further in rice crop NH_4^+ -N in soil treated with NCPCs remained significantly higher than the urea treatment, at same level of fertilizer. The applied N remained adsorbed in the form of NH_4^+ -N under flooded condition and is the predominant and preferred form of N in flooded soil (George *et al.*, 1992); it adsorbs on the soil colloids, stays longer and easily available within the root zone (Cassman *et al.*, 1998). There is also less possibility of NH_4^+ -N changing to NO_3^- -N under flooded conditions (Vlek and Byrnes, 1986).

The higher N output during the wheat growing season suggested less loss of N from the wheat field. Lower NO_3^- -N maintained by the NCPC treatments than urea because of slow release property of NCPC resulted in higher uptake and also NO_3^-N considered as the preferred form of N for uptake by wheat. During nitrous oxide emission study it was found that cumulative N_2O emission was reduced by 8.1%, 9.6% and 12.4% in WF, Na-Alg and AA+Am NCPC treated plot as compared to urea at same level of N (75% of RDF). Devkota *et al.* (2013) reported no loss of N from the wheat field because of exhausted soil fertility during the wheat growing period, i.e., reduction of soil total N at wheat harvest compared to seeding which resulted in higher N output than input during the growing season.

5.3.9 Soil organic carbon (SOC) and total nitrogen (TN)

The organic carbon was found to be important in agricultural soil because of its impacts on soil quality and agronomic production. Carbon is required in the photosynthesis process and low level of the carbon in the soil act as limiting factor on the plant growth (Srinivasarao *et al*., 2012). Results showed that organic carbon and TN was higher in the AA+Am NCPC (T_9) treated soil after harvesting in both rice and wheat crops than the control sample. The carbon was 3.45g kg^{-1} in control in case of rice soil sample and 4.12 g kg^{-1} in T_9 treated soil, whereas, for wheat 3.38g kg^{-1} in control and 3.96 g kg^{-1} in T_9. Further, among the three NCPCs higher OC was observed in AA+Am NCPC because it contains higher amount of OC (46.63%, as observed in SEM-EDX findings) but are recalcitrant in nature which delayed the C-mineralization process and able to sequester more carbon than other NCPCs. Similar finding was reported by Kaith *et al*. (2016) where they found that degradation of nanocomposites in soil do not cause any harsh effect on the nature of the soil. Moreover, % carbon contents were found to increase, which enhanced the fertility of the soil (Kaith *et al*., 2016). However, being a short-term experiment, we can not expect much change in SOC as experienced in the long-term fertilizer experiments (Rakshit *et al*., 2015). Higher amount of N recorded in NCPCs treated soil after harvesting because of their slow release behavior of nutrients. Application of higher dose of urea significantly increased the soil organic carbon in both the crops. Halvorson *et al*. (1999) observed that increase in SOC with N application reflected the responseof crop biomass to added N. More biomass production also led to greater amount of root exudation, which also increased the SOC content. Kanchikerimath and Singh, (2001) reported that increase in SOC with the application of inorganic fertilizer nutrients was because of greater input of root biomass due to better crop productivity. The favorable effect of soil organic matter on crop productivity attributed to soil water holding capacity, nutrient availability for plants, improvementof soil physical properties and efficiency of fertilizernutrients by organic amendments (Benbi *et al*., 1998). All these parameters for better crop productivity were enhanced when we applied nitrogen through superabsorbent nanocomposites in our study. Hence, biodegradation of the NCPC in the soil do not threat the fertility of the soil, rather it enhanced the soil fertility. Moreover, spontaneous growth of photo-dependent and free-living blue green algae (BGA) is a basic feature in the rice fields. Growth of these microbes and subsequent decompositionof their biomass contributes to larger SOC in rice soil (Banerjee *et al.*, 2006). Moreover, slower decomposition oforganic matter in rice soil under anaerobic condition reduced loss of carbon asCO_2resulting in larger organic carbon accumulation (Banerjee *et al.*, 2006).

The C: N ratio is indicative of the capacity of the soil to store and recycle nutrients (Al-Kaisi *et al.*, 2014).The values of SOC/TN ratio of the soils ranged from 8 (T_2) to 12.07 (T_1) in wheat and from 7.57 (T_2) to 12.77 (T_1) in case of rice crop, all other treatments gave significantly different SOC/TN than control (T_1) in both crops (Table 4.17). The C/N ratio in soil is determined by the state of organic matter, and microbial populations and activities in soil.

5.3.10 Soil microbial biomass C and N

The result suggested that reducing N fertilizer by 25% and applying biopolymer through NCPC (WF and Na-Alg) could effectively improve the microbial biomass C in both rice and wheat soil. The result showed that, in comparison with no N treatment, three NCPC fertilizer applications increased the soil enzymatic activity and MBC and MBN significantly in both rice and wheat. MBC and MBN in NCPCs @ 75% RDF were significantly equal with urea (@100%). Particularly in WF and Na-Alg NCPC the MBC was increased significantly. Baldrian *et al.*, (2011) reported that biopolymers (starch, polysaccharide and chitosan etc.) contain labile C which is easily biodegradable and represents a source of C for soil microorganisms. Kandeler *et al*. (1999) reported that application of organic manure and inorganic fertilizer together resulted in increased soil microbial biomass as manure contains vast quantities of readily utilizable energy sources, and fertilizers are rich in available nutrients. Hence, we obtained higher MBC in WF and Na-Alg NCPCs. Microbial biomass carbons were higher after the rice season than after the wheat season. This increase was caused by the seasonal temperature change, and higher temperature is known to stimulate biological activity, the decomposition of organic C and the release of DOC from soil organic matter (Kalbitz *et al.*, 2000& Clark *et al.*, 2009). Due to low temperature in winter, the number and activity of microorganisms fall down, and as the soils warms up in summer, they increases in number as well as activity (Kaur *et al.*, 2014). Therefore, more microbial population was observed in rice crop as compared to wheat crop. High microbial population in rice crop can be attributed to presence of high moisture content and temperature of the soil considerably affect the microbial content of the soil and the rhizosphere, since these factors can essentially change the amount and the pattern of nutrient secreted by plant roots (Kaur *et al*., 2014).

Further, Rakshit & coworkers,(2015) reported that level of mineral fertilization markedly affect the content of MBC in soil.They found that application of super-optimal fertilizer has increased the MBC from 218.91 µg g^{-1} dry soil (100% NPK) to 244.45 µg g^{-1} dry soil (200% NPK) at CRI stage, 230.17 µg g^{-1} dry soil (100% NPK) to 261.61 µg g^{-1}dry soil (200% NPK) at anthesis stage and from 203.27 µg g^{-1}dry soil (100% NPK) to 207.82 µg g^{-1}dry soil (200% NPK) at maturity stage.

The ratio of microbial biomass C to SOC indicates the proportion of the organic carbon that may be readily metabolized. The MBC/SOC ratio isconsidered to reflect the substrate availability in the soil microflora, or the portion of recalcitrant organic matter in the soil. Therefore, the MBC/SOC ratio provides a measure of organic matter dynamics (Anderson and Domsch 1989). The higher MBC/SOC ratio also indicates that a higher amount of organic matter is mineralized (Sparling 1992), which is interpreted as substrate available and the portion of total SOC immobilizedin microbial cells (Yang *et al*. 2010). MBC/SOC ratio in soil generally is in the range of 1–5% (Jenkinson and Ladd 1981). The microbial biomass C account for the SOC contents in present study (Table 4.19) were in agreement with those reported by Kanchikerimath and Singh (2001) who found that microbial biomass C generally comprised 3.2 to 4.8% of SOC when they applied balanced inorganic fertilizer along with manure.

The ratio of microbial biomass N to total N represents the mineralizable N fraction, i.e. it expressesthe potential of inorganic N available in the soil (Frazão *et al*., 2010). In our study theratios of microbial biomass N to total N in rice and wheat crops were 5.21% to 6.45% and 4.72% to 5.67%, respectively (Table 4.19) and also were generally within the ranges in cropland ecosystems, which were usually 2.64-3.68% observed by Haripal and Sahoo (2014) in different age series of abandoned rice field and 7.1-8.6% observed by Kanchikerimath and Singh (2001) in maize-wheat-cowpea cropping system.

The microbial quotient (MBC/MBN) represents the status of microbial community in soil. It has been reported that, higher value of MBC/MBN showed fungal dominated microbial community and lower value showed bacterial dominated microbial community in the soil ecosystem (Campbell *et al.* 1991).The ratio of MBC/MBN (4.00- 4.82) in rice (table 4.18) and 4.95- 5.73 in wheat (table 4.18) was close to the finding of Lu *et al.* (2013). Usually fungal dominated microbial community is equated with relatively more nutrient conservation mechanism in tropical soil (Haripal and Sahoo, 2014).

5.3.11 Enzyme activities

Dehydrogenase activity is an important component of the enzymatic system of every microorganism, an indicator of soilredox status and participates in microbial respiration, andtherefore, it is considered a suitable indicator of soil qualityand microbial activity. In our study the best result of DHA was reflected under application of WF NCPC @ 75% N of RDF (Table 4.20). The results were in agreement with the findings of other researchers (Kanchikerimath and Singh 2001; Masto *et al.*, 2007) who reported DHA was found highest under integrated application of organic manures and chemical fertilizers. As with microbial biomass C, optimum and balanced application of nutrients led to significant increase in dehydrogenase activity. Studies conducted by Marinari *et al.* (2000) and Kautz *et al.* (2004) reported that dehydrogenase activity was less influenced by mineral nitrogen fertilization. Dehydrogenase activity basically depends on the metabolic state of the soil biota .Dehydrogenase activity is usually enhanced by labile organic matter (Serr-Wittling *et al.*, 1996).Greater dehydrogenase activity under 75% N RDF through NCPC (WF and Na-Alg) in both rice and wheat as compared to 100% RDF confirmed the negative impact of mineral fertilizer on the enzyme (Table 4.20). It was reported that dehydrogenase activity was inhibited by large amount of fertilizer in a long term experiment (Simek *et al.*, 1999; Saha *et al.*, 2008).

A significant effect of different treatments on the activity of both alkaline and acid phosphatase in the soil was found. In the present study highest phosphatase activity recorded in 75% N RDF through WF and Na-Alg NCPC treatments was on par with the application 100% N applied through urea in both rice and wheat crops (Figure 4.33 and 4.34). This result was in line with the findings of Srilatha *et al.* (2013). Dodor and Tabatabai (2003) found that higher phosphatase activity in soil resulted from higher organic C contents in the soils. Owing to the slight alkalinity of the soil pH in this study the activities of alkaline phosphatase were higher than those of acid phosphatase. Earlier studies also proved that phosphatase activity was strongly influenced by soil pH (Dick, 1994). Optimum soil pH for alkalinephosphatase activity is 9.0–11.0, and 4.0–6.5 for the acid phosphatase (Dick and Tabatabai, 1984; Wittmann *et al.*, 2004). Jordan *et al.* (1995) suggested that acid phosphatase activity might be an appropriate measurement as an indicator of relative soil microbial activity. This is important, since most acid phosphatase are supposed to be entirely derived from soil microbial population (Frankenberger and Dick 1983).The acid phosphatase activity was lowest in 100% N alone, indicating that balanced nutrition of crop is responsible for better proliferation of root and for maximum activity of enzymes. Kanchikerimath and Singh (2001) found that the balanced amount of fertilizer nutrients and manure improved the organic matter status of soils which wasin turn reflected in the higher enzymatic activity.

One of the most important facts regarding nitrogen fertilizer is the hydrolysis of urea into CO_2 and NH_3 in soil which is catalyzed by the activity of urease enzyme. Significantly lower urease activity was found under pot receiving N fertilizers @ 100% N RDF as compared to WF and Na-Alg NCPC @ 75% N RDF. Mohammadi, (2011) found that application of nitrogen fertilizers significantly decreased urease activity while addition of organic manure increased its activity. The authors concluded that because the nitrogen fertilizers used in the experiments contained NH_4^+ and that the reaction products of urease being NH_4^+, microbial induction of urease activity had been inhibited. The effect of organic amendments on enzyme activities is probably a combined effect of a higher degree of stabilization of enzymes to humic substances and an increase in microbial biomass with increased soil carbon concentration (Martens *et al.*, 1992; Crecchio *et al.*, 2001).

On comparison of enzyme activities of rice and wheat crop, more enzyme activities were observed in rice crop as compared to wheat (Table 4.20). More enzyme activity in rice crop is also due to high moisture content in rice crop (flooding condition in rice crop). Results are in agreement with the study conducted by Banerjee *et al.* (2000) and Brzezinska *et al.* (1998). According to them, soil water content and soil temperature influence soil dehydrogenase activity by affecting the soil oxidation-reduction status. Ross and Roberts (1970) also reported that dehydrogenase activities vary with season and are dependent on soil temperature.

Present results are also supported by the study conducted be Yuan and Yue (2012). They also found lowest value of enzyme activity in winter.

5.3.12 Correlation matrix

Correlation studies have shown the existence of significant relationship between yield, nutrient uptake as well as different pools of carbon (MBC and SOC) and nitrogen in soil. Yields and nutrients uptake by rice and wheat were found significantly correlated with SOC and MBC, indicating that these pools have significant role in yield and nutrient uptake. The significant effects of biodegradable superabsorbent nitrogen fertilizers on N concentration of plants have previously been reported by several workers (Lyu *et al.*, 2015; Rahman *et al.*, 2008). On the other hand SOC and MBC significantly correlated to each other indicating that they maintain a dynamic relationship in soil. Mineral N and MBN were well correlated with yield and N uptake by rice and wheat. Availability of mineral N directly influences the N uptake by plants, MBN indirectly influences the nitrogen uptake by plant which may be attributed to positive correlation of mineral N and MBN with yield and N uptake. Significant and positive correlation was observed between MBC, MBN and enzymes activities, suggesting that these are the parameters that reflect the microbial activity in soil. Dehydrogenase, urease and phosphatase activity significantly correlated with yield and nutrient uptake by crops indicating that these enzymes have significant influence in nutrient transformation which contributed in yield and nutrient uptake. Microbial biomass and their activity are generally closely related because it is through the biomass transformations in which release of nutrients (C, N and P) occur. The microbial biomass also acts as small but labile reservoir for these elements. Nannipieri *et al.* (2002) found at high correlation between urease activity and microbial biomass in two amended grassland dark Chernozenic soil. Zhong and Cai (2007) found that soil organic C content and rice yield could be increased to a very limited extent through chemical fertilization. They found a significant regression relationship between grain yield plus straw and soil organic C content, and thus inferred that amendment with organic materials is essential for further improving soil fertility and increasing rice crop yield as well as increasing microbial biomass and community functional diversity.

5.3.13 N_2O emissions in rice and wheat crop seasons

The peaks in the N_2O fluxes coincided with fertilizer-N application in both the rice and wheat crop seasons. High emission of N_2O after fertilizer application in all the treatments in rice was due to formation of N_2O during nitrification of ammonium N produced by the hydrolysis of urea. Which supplied the substrate for nitrification (NH_4^+-N) and subsequently for denitrification (NO_3^--N). Emission of N_2O was more in WF NCPC after urea in both the crops due to fast release of N and also due to fast degradation as compared to Na-Alg and AA+Am NCPC.

In wheat crop after every dose of N application and supply of water N_2O-N flux increased due to availability of substrate for nitrification. Pathak *et al.*, (2001) reported that substantial increase in N_2O fluxes in wheat was observed after the applications of irrigation, which enhanced activities of nitrifiers and denitrifiers in soil. Huang *et al*. (2002) reported lower emission of N_2O in wheat field having higher soil organic carbon and nitrogen. In our study at the time of harvest we got highest SOC and TN in case of AA+Am NCPC followed by Na-Alg NCPC treatment, resulted in lower N_2O emission both in rice and wheat crop.

5.3.14 Relationship between N_2O emission and SOC and TN in soil

Several investigators reported that N_2O production derived from denitrification in various soils showed a positive correlation with soil organic C content (Arcara *et al.* 1999; Eaton and Patriquin 1989). A general understanding is that soils with high levels of organic C content have a greater propensity for N_2O formation than soils with low levels, notably after N application (Granli and Bøckman 1994). However, observations from this experiment showed the opposite behavior. Plotting seasonal N_2O emission against soil organic C content gave a negative nonlinear relationship (Figure 4.37a and 4.38a), suggesting that agricultural soils with higher organic C yield lower N_2O emissions. A possible explanation might be that higher C in soils would positively influence the reduction of N_2O to N in consequence of a higher content of electrondonors. Further, we again got negative linear relationship between total nitrogen in soil and N_2O emission because total N content is generally proportional to the soil C content. When the total N (TN) was plotted against the SOC, a positive linear relationship (r= 0.872 in rice and r= 0.857in wheat) was obtained. This result was in line with the findings of Huang *et al.* (2004). Gödde and Conrad (2000) showed that soils with the low contents of total and inorganic N produced the lowest amounts of NO and N_2O as compared to soils richer in organic and inorganic N. This may depend on the lower amounts of substrate N for mineralization. It may be postulated that the mineralization of soil N is the unique N source for microbes in unfertilized soils.

6. Summary & Conclusions

Rational fertilization is one of the key approaches toincrease crop yields and production profits. It was well known that different fertilizers and application methods would result in very different effects on crop growth, development, physiological characteristics, and yield component. At the present, fertilizers are normally applied in higher quantity for rice and wheat production, thus resulting in very low nutrient use efficiency and severe nutrient losses, which are also seriously polluting the eco-environment. Focusing on the characteristics of high nutrient use efficiency, it is an urgent task to develop new techniques for manufacturing fertilizers accordingly. One method for overcoming these shortcomings involves the use of slow-release fertilizers, which has demonstrated many advantages over the conventional types, such as decreasing fertilizer loss rate, supplying nutrient sustainably, lowering application frequency, and minimizing potential negative effects associated with over dosage. Slow release fertilizer (SRF) provides another means to reduce this menace by entrapping urea by physical or chemical reaction with a suitable environmental friendly matrix. Natural biopolymer like starch, lignin, cellulose and chitin are a few important macromolecules that provides easy source of low cost, less toxic and biodegradable matrix with multi-functional reactive groups that makes their easy use in fertilizer industry. The release of such kind of slow release fertilizer is controlled by the degradation rate, which in turn is affected by various factors, such as molecular weight of the polymer, and pH, temperature, ions and microorganisms in soil, etc. Superabsorbents are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining huge volumes of water in the swollen state. Recently, research on the use of superabsorbents as water management materials for agricultural and horticultural applications has attracted great attention and test of superabsorbents for agricultural applications has shown encouraging results as they have been observed to help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in soil, and increase plant growth rate. However, its applications in this field have met some problems because most of these superabsorbents are based on pure poly(sodium acrylate), and then they are too expensive and not suitable for saline-containing water and soils. Recently, there have been many reports on introducing inorganic clays, such as kaolin, bentonite, montmorillonite, attapulgite, and mica into pure polymeric superabsorbents in order to improve swelling property, hydrogel strengths, and reduce production costs. In the present work the so called biodegradable polymer is used as a holding polymer for the N nutrient.

Hence, present investigation entitled "**Nanoclay Polymer Composites with biodegradable polymers for controlled release of nitrogen in rice and wheat crops**" was identified to work out the effectiveness of NCPCs on providing slow release properties of urea in rice and wheat crop. In present investigation, experiments were conducted in lab and greenhouse. Firstly nanoclay polymer composites were synthesized and their characterization was done and then a greenhouse experiment was conducted to evaluate the slow release properties and effect on soil fertility by these NCPCs in soil with crops. Degradation behavior of prepared NCPCs was observed during incubation study in lab. A series of NCPCs were synthesized using different polymers *viz.*, wheat flour starch, sodium alginate and acrylic acid+ acrylamide. Free-radical aqueous solution copolymerization reaction was carried out by partially neutralized acrylic acid using ammonium persulfate (APS) as a free radical initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinking agent with bentonite clay. Subsequently, the prepared NCPCs were characterized by FTIR, XRD, SEM, SEM-EDX, TEM and water absorbing capacity in distilled water was determined. To study the effectiveness of slow release of nutrient from NCPCs in soil, incubation study was done in lab. Eight treatments consisting of factorial combinations of four fertilizer source and two levels of N (75 and 50% of RDF) and one treatment with 100% of RDF and one control without any fertilizer were selected. The experiment was laid out in a completely randomized design (CRD) with three replications.

A greenhouse pot trial was carried out in IARI during 2015-2016. The trial was to study the effects of different fertilizer treatments on yield and nutrients uptake of rice and wheat, the nutrients change of NCPC fertilizers and the N utilize efficiency, the other trial was to study the effects of different NCPCs on N_2O emission and their degradability in soil. There were four fertilizer treatments including urea (@100, 75, 50% N of RDF), Wheat flour NCPC (WF NCPC), sodium alginate NCPC (Na-Alg NCPC) and acrylic acid + acrylamide NCPC (AA+Am NCPC) @ 75% and 50% N of RDF and no fertilizer trial. The main results were given below:

- A series of novel swelling enhanced NCPCs were synthesized by using APS as a radical initiator and MBA as a crosslinker in aqueous solution.
- The results of FTIR spectra shown that graft copolymerization between –OH groups on clay and monomers took place during the copolymerization reaction, indicated the incorporation of bentonite within the polymer matrix.
- The exfoliated structure of AA+AM, WF and Na-Alg NCPC was observed by XRDtechnique.
- The highly porous structure of NCPCs formed by addition of bentonite was observed in SEM images, indicated the increased rate of water absorption of superabsorbent nanocomposite.
- SEM-EDX confirmed the presence of clay and urea in different NCPCs by analyzing elemental composition of the NCPCs.
- Nano sized clay particles were uniformly dispersed into the polymer matrix after the polymerization reaction was confirmed by TEM images.
- Fertilizer slow release in soil indicated that the fertilizer release properties of urea loaded NCPCs conformed to the standard of slow-release fertilizers.
- The grain yield of crops at 100% dose of urea increased 38% in rice and 59% in wheat over control. Whereas, AA+Am NCPC (75% RDF) increased rice yield by 37% and 60% in wheat as compared to control. AA+Am NCPC fertilizer at lower dose (50% of RDF) increased rice yield by 29% and AA+Am and Na-Alg NCPC fertilizer both increased wheat yield by 46% as compared to control.
- At lower dose (75 and 50% of RDF) NCPC resulted in significantly equal grain yield both in rice and wheat with 100% urea treatment.
- The nitrogen use efficiencies of all the investigated slow release NCPC fertilizers were higher than those of the conventional fertilizer application.
- Among the three NCPCs, the slow release AA+Am NCPC fertilizer treatment (T_{10}) showed higher apparent recovery efficiency (ARE) 56.54%, followed by Na-Alg NCPC treatment T_8 (56.31%) and WF NCPC treatment T_6 (53.11%) in rice and similar trend observed in wheat with highest ARE value in T_{10} (68.52%).
- Agronomic efficiency (AE) was found highest in T_{10} (16.26%) in rice whereas, 20.56% in wheat with T_{10}. Physiological efficiency (PE) was

observed highest 29.21% under treatment T_6 in rice and 30.88% in wheat with T_5.

- Micronutrient content (Fe, Zn, Cu and Mn) was found higher in Na-Alg NCPC treatment at 75% of RDF both in rice and wheat.
- In greenhouse experiment involving rice and wheat crop, application of NCPC maintained significantly higher availability of mineral N as compared to conventional fertilizer at same level of fertilizer.
- Among three NCPCs, AA+Am NCPC showed more soil mineral N availability and recovery efficiency, followed by Na-Alg NCPC, indicating their potential in increasing nitrogen use efficiency and decreasing nitrogen loss in rice – wheat crop.
- Lower percentage of nitrification rate was observed in NCPC treatments as compared to conventional fertilizer due to its slow release property.
- The higher unaccounted (loss) mineral N in conventional fertilizer as compared to NCPC treatments.
- Soil organic carbon and TN was higher in the AA+Am NCPC (T_9) and Na-Alg NCPC (T_7) treated soil after harvesting in both rice and wheat crops than the conventional fertilizer treatment.
- Reducing N fertilizer by 25% through WF and Na-Alg NCPC could effectively improve the MBC by 66% (T_5) and 61% (T_7) in rice and 47% (T_5) and 45% (T_7) in wheat, respectively compared to control.
- Microbial biomass N was found significantly equal at higher dose of conventional fertilizer and NCPC treatments (WF and AA+Am NCPC).
- Ratio of biomass carbon to soil organic carbon was found significantly higher in WF NCPC treatment both in rice and wheat.
- Higher MBN to total nitrogen was observed in WF NCPC in rice, whereas no significant differences were observed between the treatments in wheat. Higher percentage of MBC/SOC and MBN/TN are desirable because soil MBN and MBC may serve as an important pool of available soil C and N.
- Urease activity was highest under WF NCPC in rice and wheat, while dehydrogenase activity was highest under T_7 in wheat and under T_5 in rice. Both acid and alkaline phosphatase activity was found higher under T_5 in rice and wheat.

- More enzymatic activities were observed in rice compared to wheat due soil water and temperature difference.
- Higher N_2O emission was observed in conventional fertilizer treatment followed by WF NCPC and least was observed in AA+Am NCPC in both rice and wheat crop duration.
- A negative linear relationship was observed between the N_2O emission and SOC and TN.
- Higher CO_2 evolution was measured under WF followed by Na-Alg and then by AA+Am NCPC in both moist as well as flooded soil condition during incubation period.
- Lowest biodegradation was observed in AA+Am NCPC (11.2%), while maximum was noticed in WF NCPC (32.8%).
- Pearson's correlation studies have revealed the existence of strong relationship ($p = 0.05$ and $p = 0.01$) among most cases of soil enzyme activities, soil nutrient availability and nutrient uptake by crops.

Based on the results obtained in the present investigation, the following conclusionscan be drawn:

1. Graft copolymerization between clay and polymer took place which indicated that the clay dispersed into the polymer matrix and chemicallyreacted with the polymers.
2. NCPC fertilizer (WF) at 75 and 50% RDF could serve as a low cost fertilizer with enhanced agronomic benefits compared to conventional and other synthetic fertilizers.
3. Slow release polymer fertilizers are biodegradable in nature and have no adverse effect on the soil fertility, rather it enhance the fertility of the soil. Thus, biodegradable NCPCs are important in environmental and technological view point.

Nanoclay Polymer Composites (NCPCs) with biodegradable polymers for controlled release of nitrogen in rice and wheat crops

ABSTRACT

Composites of biodegradable polymers and nano- bentonite were chosen in the present investigation. To achieve the objectives, experiment was conducted in lab for synthesizing, characterizing and evaluating the biodegradability behavior of the NCPCs. Greenhouse pot culture experiment was carried out to study the effects of NCPC fertilizers on crop yield, nutrient uptake, soil microbial activity, nitrogen availability in soil, N_2O emission in rice (*Oryza sativa* L.) and wheat (*Triticum aestivum* L.) crops. The NCPCs were synthesized based on three different types of polymers (wheat flour starch, sodium alginate and acrylic acid plus acrylamide) via free radical polymerization in the presence of bentonite clay powder by using ammonium persulfate (APS) as a free radical initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinking agent. These nanocomposites were swollen in aqueous solution of urea to produce slow release fertilizer. The nanocomposites were characterized by XRD, FTIR, SEM, SEM-EDX and TEM. Results revealed that NCPCs were participated in the graft polymerization reaction with AA and the bentonite layers were exfoliated and basically dispersed in the composites on a nanoscale after the polymerization. At 30th day of incubation, % N release in soil reached 87.22, 59.91, 63.77 and 60% of total applied N as Urea, AA+AM, WF and Na-Alg NCPC, respectively. A laboratory incubation study was carried out for 91 days in moist and flooded soil condition to evaluate the biodegradable behavior of prepared NCPCs. Results revealed that in treatments with moistened condition increased 16.28-18.80% CO_2-C emission over flooding condition.

The result of greenhouse experiment indicated that at lower dose NCPCs (75 and 50% of RDF) the grain yield both rice and wheat was on par with 100% urea treatment. The nitrogen use efficiencies of all the NCPC fertilizers were higher than those of the conventional fertilizer application. Higher micronutrient content was found in Na-Alg NCPC (@ 75% RDF). Amongst the NCPCs, AA+Am NCPC showed higher soil mineral N availability and recovery efficiency, followed by Na-Alg NCPC, indicating their potential in increasing nitrogen use efficiency and decreasing nitrogen loss in rice – wheat crops. Highest MBC, MBN and enzymatic activities were noted in WF NCPC (T_5). Reducing N fertilizer by 25% through WF and Na-Alg NCPC could effectively improve the MBC by 66% (T_5) and 61% (T_7) in rice and 47% (T_5) and 45% (T_7) in wheat, respectively compared to control. Urease activity was highest under WF NCPC (T_5) in rice and wheat, while dehydrogenase

activity was highest under T_7 (Na-Alg NCPC) in wheat and under T_5 in rice. N_2O emission was found highest in conventional fertilizer followed by WF NCPC.Negative relationship observed between the N_2O emission and SOC (R^2= 0.86 in wheat and R^2= 0.74 in rice) and TN (R^2= 0.90 in rice and R^2= 0.97 in wheat). Pearson’s correlation studies have revealed the existence of strong relationship (p = 0.05 and p = 0.01) among most cases of soil enzyme activities, soil nutrient availability and nutrient uptake by crops, straw and grain production.

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oreku v/;;u e ck;kfMxMcy ikyhej dk puk x;kA bl mnn'; dk ijk dju d fy, i;kx'kkyk e i;kx fd; x; ftle uukDy ikyhej dEikftV dk fuek.k] x.k&fufn"Vhdj.k ,o ck;kfMxfMfcfyVh 0;ogkj 'kkfey FkkA Qlyk dh mit] ik"kd rRo dh miyC/krk] feVVh l{ethoh xfrfof/k] ukbVl vkDlkbM mRltu bR;kfn ij ¼,ulhihlh,l½ d iHkko dk v/;;u xhu gkml e ikV e fd;k x;kA rhu idkj d vyx&vyx ikyhejk ¼xg dk vkVk] lkfM;e vkythuV rFkk ,dkbfyd ,flM + ,dby vekbM½ ij vk/kkfjr Qh jfMdy ikyhejkbt'ku fof/k }kjk dkl c/kd ,u] ,u feFkkbyhu fclvdkbyvekbM] ikjHkd d :i e vekfu;e ijlYQV dk i;kx djr g, cUVkukbV uuk ikmMj dh ifLFkfr e] NCPCs dk fuek.k fd;k x;kA fufer NCPCs dk ;=hdj.k ,lb,e] Vhb,e] ,QVhvkbvkj] ,Dlvkj Mh] ,b,e&bMh, vkfn rduhdk dk i;kx djr g, y{k.k o.ku fd;k x;kA bu fufer NCPCs dk ;fj;k d tyh; ?kky e vo'kkf"kr djk;k x;k ftll dh ok ;fj;k dk /kheh xfr l NkMu d okgd d :i e dk; dj ldA i;kx djr g, y{k.k o.ku dh fofHkUu fof/k;k l efRrdk vkj cgyd d chp lgcgyhdj.k dk l>ko feyk ftll ;g irk pyk dh cgyd efVDl e mifLFkr efRrdk vkj cgydk d lkFk mudh jklk;fud vfHkfd;k l NCPCs dk fuek.k gvkA bD;clu d 30 fnu ij feVVh e dy Mky x, ;fj;k dk ifr'kr N 87-22] 59-91] 63-77 vkj 60 ifr'kr] ;fj;k] AA+AM] WF rFkk Na-Alg NCPC de'k% iklr fd;k x;kA ck;kfMxMcy 0;ogkj d eY;kdu d fy, fufer NCPCs dk bD;clu 91 fnuk d fy; tyeXu ,o ueh;Dr feVVh e i;kx'kkyk e v/;;u fd;k x;kA ck;kfMxMcy 0;ogkj d eY;kdu d ifj.kke l irk pyk fd CO_2 mRltu dh ifd;k 16-28&18-80 ifr'kr ueh ;Dr feVVh e tyeXu feVVh l vf/kd ikb xbA

xhugkml i;kx d ifj.kke l ; ldr feyk dh de Mkt ¼75 rFkk 25 % RDF½ rFkk 100 ifr'kr ;fj;k Mkt l /kku vkj xg nkuk d gh mit cjkcjh ij FkhA lHkh NCPC mojdk dh ukbVkstu mi;kx {kerk ikjifjd modj l vf/kd ikb xbA l{eik"kd rRok dh miyC/krk Na-Alg NCPC (@ 75% RDF) e T;knk ikb xbA lHkh NCPC d chp] AA+AM NCPC e mPp feVVh [kfut N miyC/krk vkj iu%ikfIr n{krk ikb xb vkj mld ckn Na-Alg NCPC }kjk ik;k x;k ftll fd budh mPp N mi;kx n{krk e of) vkj /kku&xg Qlyk e bud }kjk de ukbVkstu gkfu d {kerk dk ldr feykA feVVh d lc/k e mRre l{ethoh xfrfof/k] mPpre MBC] MBN rFkk ,tkbe xfrfof/k;k dk ldr WF NCPC (T_5) e feykA de mojd Lrj ij 25 ifr'kr WF ,o Na-Alg NCPC d i;kx u iHkkoh :i l ,echlh 66 ifr'kr (T_5)] 61 ifr'kr (T_7) /kku e rFkk 47 ifr'kr T_5 ,o 45 ifr'kr T_7 xg e de'k% fu;f=r mipkj l vf/kd ik;k x;k ;fj,t xfrfof/k] /kku ,o xg e WF NCPC (T_5) d rgr lcl T;knk Fkk] tcfd MhgkbMkstut xfrfof/k xg e T_7 (Na-Alg NCPC) vFkok /kku e T_5 lokPp FkkA ukbVl vkDlkbM dk mRltu lcl T;knk ikjifjd mojd e ik;k x;k vkj mld ckn WF NCPC e ik;k x;kA ukbVl vkDlkbM dk mRltu rFkk SOC (R^2 = 0.86) xg e R^2 = 0.74 /kku e½ rFkk TN (R^2 = 0.90 /kku e rFkk (R^2 = 0.97 xg e½ d chp udkjkRed lc/k ik;k x;kA fi;lUl dkfjy'ku v/;;u e vf/kdk'k ekeyk e feVVh e ,tkbe xfrfof/k;k] feVVh e ik"kd rRok dh miyC/krk vkj Qlyk }kjk ik"kd rRo dh ikflr d chp etcr fj'r (P = 0.05 vkj (P = 0.01) d vfLrRo dk irk pyk gA

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