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Fixation of Urea to Polyacrylic Acid and Nitrogen Release Behavior of the Product (Polyurea)-A Comparison with Urea and Control (Without Nitrogen Fertilizer)*

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Abstract: A slow-release nitrogen fertilizer was prepared by covalently immobilizing urea on a biodegradable acrylic acid based polymer matrix. Polyacrylic acid was prepared by solution polymerization of acrylic acid followed by covalent immobilization of urea through the activated carboxyl groups. The resulting product, termed as polyurea, was characterized by FTIR and NMR spectral analyses, thin layer chromatography measurement and elemental analyses. Results showed that polyurea contained 24.76% nitrogen and the solvency reduced to over 300 times as compared to urea. To clarify the performance of this polyurea in agriculture, a comparative study was then carried out on the growth of green chili *Capsicum annuum* plants using urea and control (no nitrogen fertilizer) as the basis. Polyurea showed improved yield in terms of average plant size over the cultivation period. The nitrogen release behavior in soil during cropping and plant uptake of nitrogen suggested that polyurea can be used as slow-release nitrogen fertilizer.

Key words: Slow-release, polyurea, urea, nitrogen, green chili plants

INTRODUCTION

Nitrogen is one of the primary macronutrients essential for cultivation. The most important and commercially available nitrogen containing fertilizer is urea because of its high nitrogen content (45-46%) and relatively low cost of production (Liu *et al*., 2006). However due to high surface run off, leaching and vaporization the utilization efficiency or plant uptake of urea is generally below 50% (Abraham and Pillai, 1996). The loss of urea particularly in flood prone areas creates not only huge economic loss but also environmental pollution (Al-Zahrani, 2000; Akelah, 1996). Moreover the rapid release of nitrogen is also associated with rapid plant growth, often favoring the fast growth of weedy species over native plants causing the fast depletion of nitrogen capacity of the fertilizer (Claassen and Carey, 2007). Recently synthetic controlled-release fertilizers are getting much attention because of these environmental and economic concerns. Controlled-release or slow-release fertilizers basically demonstrates many advantages over the traditional type, such as decreased rate of losses of fertilizer from soil by rain or irrigation water, sustained supply of nutrient for a prolonged time, maximized uptake and utilization efficiency of the nutrient, lowered frequency of application, minimized potential negative effects on the environment from over dosage and reduced toxicity (Tomaszewska and Jarosiewicz, 2002; Guo *et al*., 2005, 2006).

Controlled-or slow-release fertilizers are broadly divided into uncoated and coated products. Uncoated products rely on their inherent physical characteristics, such as low solubility, for their slow release. Coated products mostly consist of quick-release nitrogen sources surrounded by a barrier that prevents the nitrogen from rapid release into the environment. Superabsorbent composites, a three-dimensional crosslinked hydrophilic polymer network, capable of holding large amount of water in the

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swollen state can be useful for the release of water soluble agrochemicals through the coated barrier (Saraydin *et al*., 2000). A number of researchers reported the preparation of such superabsorbent composites based on acrylic acid and studied mostly the water absorbency or water retention capacity with varying conditions like temperature, pH etc. or composition (Li *et al*., 2005; Zhang *et al*., 2005; Chen and Zhao, 2000). However none of these works included any field applications. The rate of nutrient release from the coated products is determined by the composition of coating, coating thickness and sometimes crosslinking density. Moreover the preparation of most of these coated fertilizers requires complicated and lengthy process which leads to often high valued ultimate product (Alva and Tucker, 1993; Jarrell and Boersma, 1979; Shaviv and Mikkelsen, 1993). However uncoated fertilizers had some advantages over the coated fertilizers. Comparatively the distribution of nitrogen in uncoated fertilizers is homogeneous and nitrogen release rate is independent of coating.

In the present investigation, the main objective is to covalently fix urea to a polymer matrix consisting of polyacrylic acid (PAA) through activation of carboxyl groups. We called this product as polyurea. Since the availability of nitrogen in soil is directly related to the growth of plants so in the application phase plant growth responses of green chili plants to polyurea were investigated. The results were compared with those obtained from plots containing urea and no nitrogen fertilizer labeled as control. The release pattern of nitrogen in soil during cropping and nitrogen content in different plant parts were also measured for three different treated soils.

MATERIALS AND METHODS

Materials

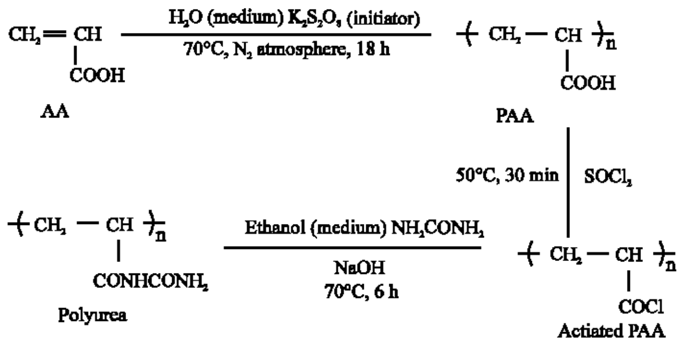
Acrylic acid (AA) of monomer grade (Fluka Chemika, Switzerland) was distilled under reduced pressure and preserved in the refrigerator until use. Potassium persulfate (KPS) of reagent grade was recrystallized from distilled water at low temperature and preserved in the refrigerator before use. Commercial grade urea and thionyl chloride (BDH, England) were used without any purification. Other chemicals used were of reagent grade. Distilled deionized water was used for all the measurements.

The whole measurement was conducted at the Department of Chemistry of Rajshahi University, Bangladesh during Kharip season (January 06, 2007 to May 30, 2007).

Preparation of Polyurea

PAA was prepared by polymerizing 30 g of AA taken in a three necked round bottom flask dipped in a thermostated waterbath maintained at 70°C. The polymerization was carried out in presence of 100 g water containing 0.6 g of KPS as initiator. This reaction was continued for 18 h in a nitrogen atmosphere. At the end of reaction, PAA solution was reduced to half its initial volume simply by boiling, cooled to 5-6°C and then 65.5 mL of thionyl chloride was added dropwise over a period of 1 h. After complete addition of thionyl chloride temperature was raised to 50°C and heating was continued for another 30 min. The activated chlorinated product of PAA was precipitated, filtered and dried at a reduced temperature in a desicator over $CaCl_2$. In the final step, 5 g of chlorinated PAA was taken in a round bottom flask containing 300 mL ethanol, 10 g urea and 0.5 g NaOH. The content of the flask was heated under reflux at 70°C for 6 h. The product polyurea was precipitated from ethanol and washed repeatedly with ethanol to remove urea. Synthetic route for the preparation of polyurea is shown in Scheme 1.

Polyurea was characterized by thin layer chromatography (TLC) measurement, FTIR (SHIMADZU-FTIR 8900, Japan) and ^{1}H NMR (BRUKER 400 MHZ Ultra shield™ NMR, Switzerland) spectral analyses. The content of nitrogen was measured by the Kjeldahl method (AOAC, 1990). Table 1 shows some physical characteristics of urea and polyurea.



Scheme 1: Preparation of polyruea

Table 1: Properties of urea and polyurea

Physical Properties	Urea	Polyurea
Nature (At ambient temp.)	Solid	Solid
Nitrogen (%)	46.66	24.76
Molten temp. (°C)	115-120	80-85
Solubility (g/100 mL) (At ambient temp.)	104	0.3

Soil Preparation and Fertilizer Application

Plantation was carried out in earthen pot of 24 cm height and 30 cm diameter with a hole at the centre of the bottom to drain out excess irrigation/rain water. Each pot contained 12 kg of soil (sandy loam, pH 7.9) with total soil area 0.07 m^2. Before plantation soil of each pot was thoroughly mixed with 1.52 g triple superphosphate, 0.94 g muriate of potash and 0.5 g gypsum. In each pot three green chili plants of 12-13 cm height (approximately 1 month old) were then planted on January 06, 2007. After 30 days of plantation i.e., on February 05, 2007, 1.07 g urea and 1.88 g polyurea were applied respectively in urea and polyurea treated pots, at around 2 cm depth and distance surrounding the plants, the quantities being estimated on the basis of percentage of nitrogen content (Table 1) of the fertilizers and the optimum value of nutrient required for chili plant (Bangladesh Agricultural Research Council Repts., 1997). Four pots were used for each of polyurea, urea and control (without nitrogen fertilizer). Plant height (from ground level to the tip of flag leaf) and number of leaves were measured during plant growth from time to time.

It is important to note that during this whole experiment, pots were maintained in open air with temperature and humidity averaged between 18.1-29.5°C and 55.5-91.58%, respectively and total rainfall was recorded as 198 mm. Watering of the soil was done at the identical level in each pot as when the soil was visibly dried.

Nitrogen Content in Soil and Plant

Nitrogen content in the soil was measured by Kjeldahl method (AOAC, 1990) during cropping at different time intervals, started after 10 days of fertilizer application. For this measurement a homogeneous soil sample was first prepared by random sampling from three different spots down to a depth of around 2 cm of each treated pot. Average nitrogen content in leaves was also measured during plant growth by the same method. For this measurement three leaves were collected from each plant from time to time. After 140 days of cropping (May, 31, 2007), plants were taken off, dried and ultimate nitrogen levels in different plant parts such as matured chili, stem and root were measured.

Data Analysis

The values of F ratios were calculated for plant height and number of leaves using randomized block design for different treatments such as polyurea, urea and control. ANOVA was used for this purpose. Duncan's New Multiple Range Test (DMRT) was also used to identify the performance of different treatments on plant height and number of leaves. Similar analysis was also made for nitrogen content in polyurea, urea and control treated soils.

RESULTS AND DISCUSSION

In the FTIR spectra of both urea and polyurea, broad absorption signal due to N-H stretching appeared between 3200-3500 cm^{-1} and a signal due to C = O appeared between 1600-1700 cm^{-1}. Polyurea gave two absorption signals due to $N\text{-}H_2$ and N-H bending at 1455.2 and 1404.1 cm^{-1} respectively while in urea one such signal due to $N\text{-}H_2$ bending appeared. The absorption band due to alkyl part of polyurea appeared in the range between 1333.7 and 1072.3 cm^{-1}. Figure 1 shows the FTIR spectra for urea and polyurea.

In the ^1H NMR spectra of polyurea, the chemical shifts due to amide ($-CONH_2$) and substituted amide (-CONH-) are observed at 2.19 and 4.12 pm, respectively. Chemical shift due to carboxyl (-COOH) is not visible in the region 10.5-12 ppm indicating that carboxyl group is completely eliminated by substituted amide linkage due to the covalent bonding with urea. The ^1H NMR spectra of polyurea is shown in Fig. 2. It was difficult to assign all the chemical shifts appeared in the NMR spectra, because macromolecules in solution tend to have complicated chemical structure resulting from inter and intra molecular hydrogen bonding. The shielding/deshielding effect may therefore produce multiple chemical shifts due to methylene/amide group protons.

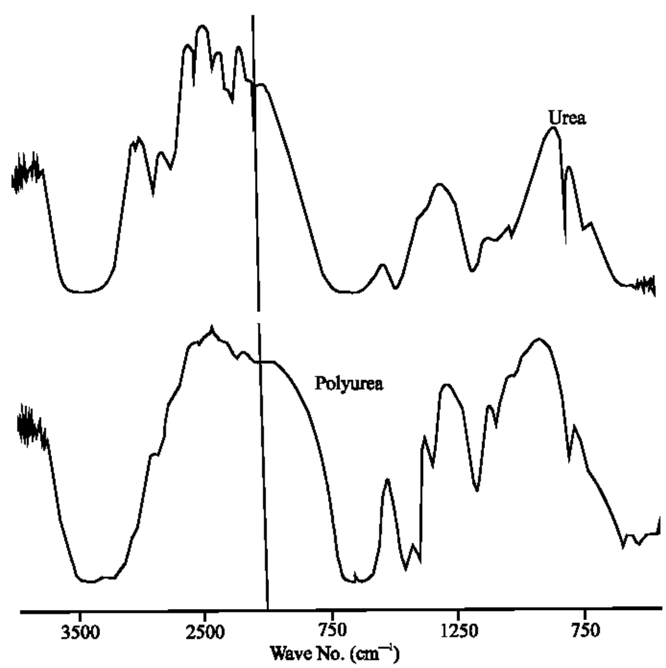


Fig. 1: FTIR spectra of urea and polyurea

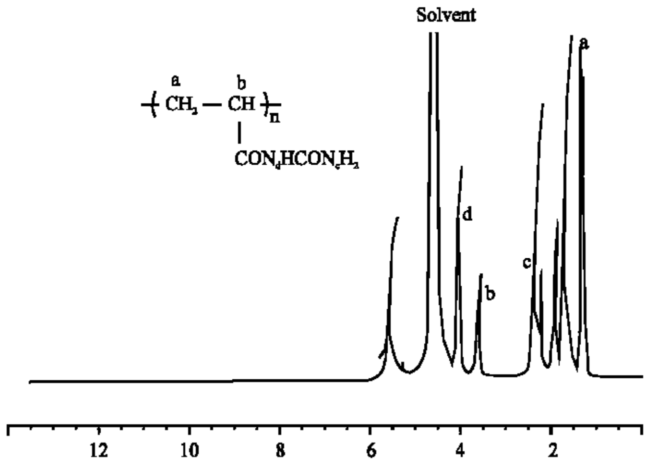


Fig. 2: ^{1}H NMR spectra of polyurea in D^2O

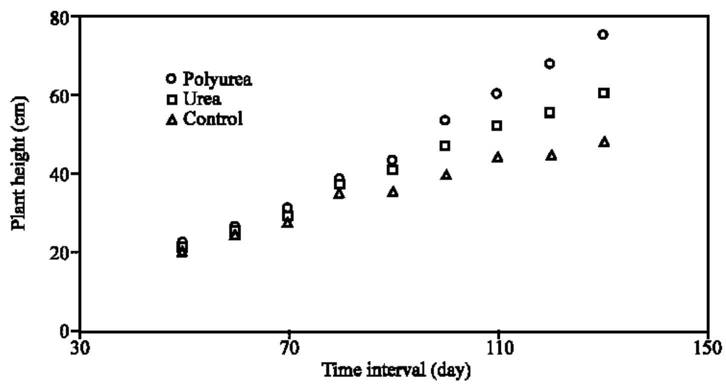


Fig. 3: Variation of average height of chili plant measured at the interval of ten days during plant growth in urea, polyurea and control treated earthen pots

TLC measurements of urea and polyurea were carried out in a mixed solvent of methanol and petroleum ether (1:1). Both urea and polyurea gave sharp single spots with different R_f values of 0.918 and 0.891 for urea and polyurea respectively. The nitrogen content in polyurea measured by Kjeldahl method was found to be 24.76% which is very close to the theoretical value (24.56%). The above spectral and elemental analyses suggest that urea is successfully linked covalently to the polyacrylic acid.

Solubility is an important parameter that determines the performance of a slow-release fertilizer (Dou and Alva, 1998). Solubility measurement indicates that large volume of water is necessary to dissolve polyurea (Table 1) and the dissolution process was also relatively slow, taken six days. The first stage in polymer dissolution was characterized by swelling due to the slow penetration of the water molecules into the interstices of the polymer matrix. As swelling continued more and more segments of the polymer molecules were solvated and loosened out. The loosened polymer molecule then diffused slowly out of the polymer matrix and dispersed in the water phase resulted in a completely homogeneous solution after six days. This slow dissolution and relatively low solubility of polyurea may be taken as an important prerequisite for being applicable as a slow-release fertilizer.

Figure 3 shows the average plant height of chili plant in each polyurea, urea and control treated pot. The height was measured after plantation at the interval of 10 days. In all cases the plant height

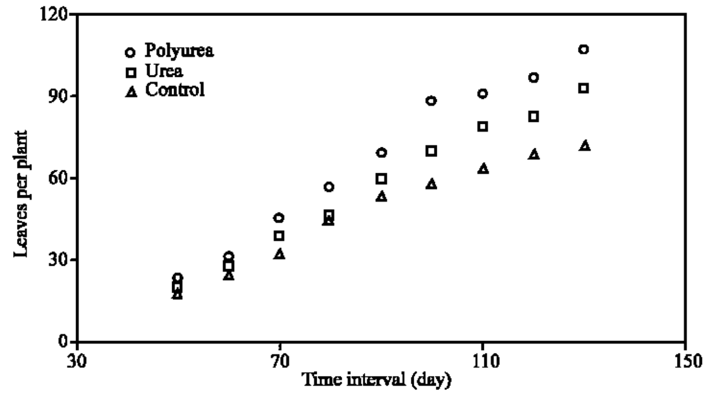


Fig. 4: Variation of average number of leaves per chili plant measured at the interval of ten days during plant growth in urea, polyurea and control treated earthen pots

increased with passing of time. However, in polyurea treated pot the average plant height increased at a faster rate after 80 days of plantation (i.e., after 50 days of fertilization) relative to that in the urea treated pot. In absence of urea (control) the plant height increased but relatively at a lower rate. The statistical analysis for this measurement shows that the calculated value of F-ratio is greater than the tabulated value of F at 5% level of significance. This implies a difference among the resultant plant heights with the variation in soil treatments. Moreover, mean difference values of both polyurea (11.71) and urea (6.03) from control are greater than the values of least significant difference (LSD) at both 5% (4.31) and 1% (5.94) level of significance. Another important observation is that the mean difference value in case of polyurea is higher than that of urea. Hence statistical analysis suggests that polyurea increases the average height of chili plant relative to others.

The average number of leaves were also measured at different time intervals per chili plant in polyurea, urea and control treated pots. As shown in Fig. 5, the average number of leaves increased with time after plantation. Figure 5 also shows a similar trend as observed in Fig. 3, that is in polyurea treated pot the average number of leaves increased more rapidly than in urea treated pot. It may be mentioned that all the pots under experiment were subjected to the same environment with controlled irrigation and rain water. Therefore it can be assnmed that the apparent increase in the growth of chili plant in polyurea treated pot is due to the sustained and slow release of nitrogen. Data analysis suggests that mean difference value of polyurea from control (19.289) is greater than LSD values at both 5% (5.37) and 1% (7.40) level of significance. Moreover the mean difference value of polyurea from urea (10.23) is greater than LSD values at both 5 and 1% level of significance. Therefore from this analysis it can be predicted that polyurea relatively increases the growth of plants.

In order to study the release behavior of nitrogen in soil, the nitrogen content in polyurea, urea and control treated soils were measured at various time intervals after plantation. It may be mentioned that fertilizers were applied after 30 days of plantation and nitrogen level in the respective soil was measured after 10 days fertilizer application. Figure 5 shows the variation of nitrogen content in polyurea, urea and control treated soils. Before plantation the nitrogen content in the soil was 0.09%. Initially i.e., after 10 days of fertilizer application polyurea treated soil has the highest nitrogen content followed by urea and control. Relatively the low nitrogen level in urea treated soil is expected to be due to the surface runoff, evaporation and leaching (Abraham and Pillai, 1996). However, the initially higher nitrogen content in polyurea treated soil is derived from the combined effects of relatively low solubility, strong adhesion of macromolecular chain with porous soil particles and hence less vaporization and poor leaching of the covalently bonded urea. Many researchers also reported improvement in growth and nitrogen uptake by seedlings using different types of slow-release fertilizers (Krasowski *et al*., 1999). However, it would be unwise to compare the values as the uptake is always influenced by the soil pH, moisture and temperature etc. (Shaviv and Mikkelsen, 1993). In

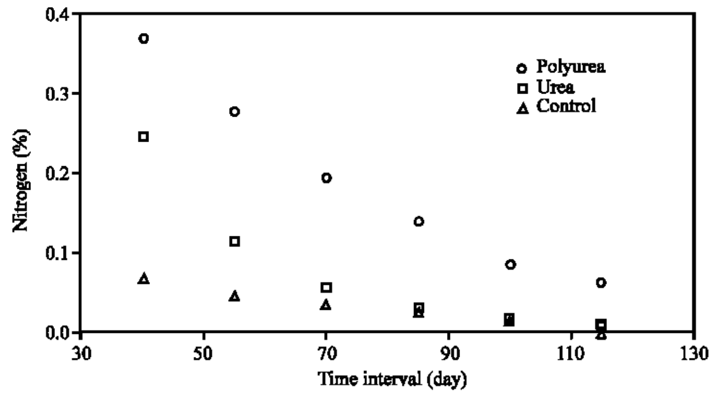


Fig. 5: Variation of average nitrogen content in polyurea, urea and control treated soils measured at different time intervals during plantation

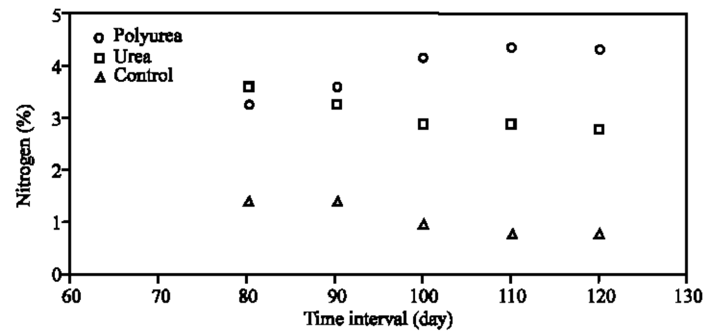


Fig. 6: Variation of average nitrogen content in the leaves of chili plant collected at different time intervals from polyurea, urea and control treated soils

both urea and control treated soils, nitrogen content reduced rapidly and reached very low level in the middle of the cropping season while in polyurea treated soil nitrogen content reduced steadily. It is also observed that at the end of cropping season trace (0.064%) nitrogen is available in polyurea treated soil whereas in urea and control treated soil nitrogen content reduced to almost zero. The optimum solubility of polyurea in water is important as it determines the availability of nitrogen for plant uptake. An important characteristic of all good control-release fertilizers is that most of the nutrient should be available throughout the entire test season rather than remain in the soil for the next crop season (Claassen and Carey, 2007; Oertli, 1980). The decreasing tendency and ultimate value of nitrogen in polyurea treated soil showed that only trace nitrogen is available for the next crop and this is almost equivalent to the nitrogen content before plantation (0.09%). This behavior suggests that polyurea can be utilized as control-release nitrogen fertilizer. A statistical analysis was also performed on the data of nitrogen content in soil obtained at different time interval during cropping. The mean difference value of polyurea (0.1565) from control is greater than LSD values at both 5% (0.0669) and 1% (0.0951) level of significance but the mean difference value of urea (0.0466) from control is lower. Again the mean difference value of polyurea from urea (0.109) is higher than the LSD values at both 5 and 1% level of significance. Hence this analysis also supports the early observation that is in case of polyurea, nitrogen availability in soil is higher than urea for plant uptake during cropping.

The uptake of nitrogen by the plant was determined by measuring the average nitrogen level in leaves at different time interval during plant growth. Figure 7 shows this variation of nitrogen level in leaves with time. Interestingly the nitrogen level in the leaves collected from plants planted in urea and

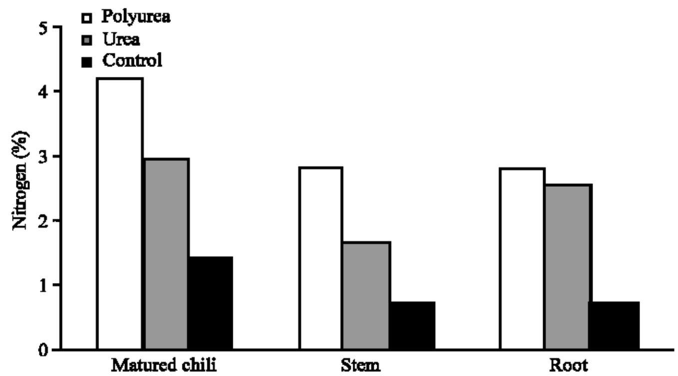


Fig. 7: Bar diagram of average nitrogen content in matured chili, stem and root measured after de-plantation from urea, polyurea and control treated soils

control treated soils decreased with time whereas in polyurea treated soil it increased with time. This may suggest that plant is receiving nitrogen continuously at such a rate from polyurea treated soil that it causes accumulation of nitrogen. The decrease in nitrogen level in urea and control treated soil imply that plant is suffering from nitrogen deficiency.

Similarly the nitrogen level in matured chili, stem and root were also measured. It may be mentioned that stem and root were collected after de-plantation at end of cropping. Figure 7 shows the comparative bar diagram for plant parts obtained from three different soils. The nitrogen content in all three plant parts obtained from polyurea treated soil indicates relatively higher value. This result again suggests that the use of polyurea maximizes the uptake of nitrogen from soil. Hence polyurea has the potential to be used as control-release fertilizer.

CONCLUSION

Polyurea was prepared by covalent binding of urea with polyacrylic acid followed by activation of carboxyl group. The solubility of polyurea decreased 300 fold as compared to urea. Polyurea did not produce any toxic effect on the growth of plant as evident from the increased growth rate of plant measured in terms of average-plant height and number of leaves. The release behavior and plant uptake of nitrogen greatly improved in case of polyurea treated soil. These observations suggest that the synthesized polyurea produced sustained and slow-release of nitrogen during plantation and also minimized the loss of nitrogen through surface run-off, vaporization and leaching.

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