



RESEARCH PAPER

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Preparation of polymer matrix and release patterns of nitrogen from the product

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Abstract

Nitrogen fertilizers used to grow agricultural crops around the globe have a great problem. After they are applied to the soil, more than three quarters of their nutrients get washed away before plants can absorb them. Urea is a common source in nitrogen. But it is quickly breaks down into ammonia, which creates environmental pollution and chemical hazards. In this research we prepared a slow release nitrogen fertilizer that release nutrient overlong period of time giving crops more time to absorb them, which also reduce to loss of urea to the environment. A slow-release nitrogen fertilizer prepared by covalently immobilizing urea on a biodegradable polymer matrix consisting of Poly (Methacrylic acid)(PMAA). The resulting product abbreviated as PMAU, was characterized by FTIR and NMR spectral analyses, thin layer chromatography measurement and elemental analyses. Results showed that PMAU contained 32.85% nitrogen and the solvency reduced to over 335 times as compared to urea. To clarify the performance of PMAU in agriculture, a comparative study was carried out on the growth and development of green chili '*Capsicum annuum*' plants using urea and control (without N-fertilizer) as the basis. The release profiles of nitrogen in soil and plants were examined. Release rate of nitrogen was slow and steady in PMAU treated soil than urea treated soil under same condition. The growth of chilli plants was relatively faster in presence of PMAU. The experimental data indicated that the product can effectively reduce nutrient loss, improved the use efficiency of water and prolong irrigation cycles in drought prone environments.

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Introduction

There are seventeen elemental nutrients required for plants growth and development. Among them nitrogen is one of the most essential macronutrients for plant (John *et al.*, 2005). A wide variety of N fertilizers are used by the agriculturists, but because of the relatively higher N content (45-46%), ease of production and low price, urea has gained popularity among the farmers. Urea is a highly soluble and to some extent volatile compound causing high surface runoff, leaching and vaporization. This ultimately reduces the utilization efficiency of the fertilizer by the plant below 50% (Abraham and Pillai, 1996). The loss of urea to the air and water stream may cause serious environment pollution as well as economic loss (Akelah, 1996 ; Ko *et al.*, 1996; Al-Zahrani, 2000; Guo *et al.*, 2005). In order to overcome these problems researchers, particularly in the developed countries, are concentrating on new technology dealing with sustainable and control/slow fertilizers (CRF/SRF) (Christianson, 1988; Kochbu *et al.*, 1990; Raigon *et al.*, 1996; Huett *et al.*, 2000; Yanfeng *et al.*, 2004; Guo *et al.*, 2006; Claassen *et al.*, 2007). Over the traditional type CRFs offer advantages like decreased rate of nutrient loss from soil by rain/irrigation water, sustained release of nutrient for long time, maximized uptake and utilization efficiency of the nutrient, lowered frequency of application, minimized negative effects on the environment from over dosage and reduced toxicity (Shaviv *et al.*, 1993; Tomasezeska *et al.*, 2002; Mingzhu *et al.*, 2006). The farmers in Bangladesh are mostly illiterate. In order to obtain high production they often apply excess urea without analyzing nutrient level in the soil. Moreover, the soil composition and climate in Bangladesh are different and is frequently affected by flood. Therefore, the excess use of urea by farmers multiplies their economic loss and environmental pollution. It has been reported that the release rate of nutrient from CRFs is affected by microbial activities in soils as well as by their physical and chemical properties (Shaviv *et al.*, 2003). Attempts have therefore been made in this study to develop new CRF that would maintain the nutrient level in soil long period of time without

frequent applications. To our knowledge, there is no alternative nitrogen fertilizers to date. Therefore, it is highly desirable to prevent urea from undergoing rapid loss from soils without any influence on its fast effectiveness. This would lead to improvement of urea efficiency and consequently to reduction of nutrients losses from agricultural soils. In this research our main objective is to reduce the loss of nitrogen by covalently binding highly water soluble urea to a biodegradable polymer matrix. The polymer matrix would limit the solubility of nitrogen in water and thereby maintain the appropriate concentration in soil for long time. For this reasons in present work urea was fixed to a polymer matrix polymethacrylic acid (PMAA) through activation of carboxylic groups. The resulting product polymethacrylic urea is abbreviated PMAU was characterized by FTIR, NMR, thin layer chromatography and elemental analysis. The solubility of nitrogen in soil is directly related to growth of plants. So in application phase growth of green chili "*Capsicum annuum*" plants to PMAU was investigated. The release behavior of nitrogen in soil and subsequent plant uptake of nitrogen were also investigated and obtaining result were compared with urea and control (with nitrogen fertilizer).

Materials and methods

MAA of monomer grade, from Fluka, Chemika, Switzerland was distilled under reduced pressure and preserved in the refrigerator. Potassium persulfate (KPS) of reagent grade from LOBA, Chemika, India, was recrystallized from water at low temperature and preserved in the refrigerator. Thionyl Chloride from BDH, England and urea [NH_2CONH_2] as N fertilizer were of commercial grade. NaOH, H_2SO_4 , Na_2S all of reagents grade were used without further purification. Distilled de-ionized water having conductivity less than $5 \mu\text{S}/\text{cm}$ was used for all measurements. Other chemicals were of analytical grade.

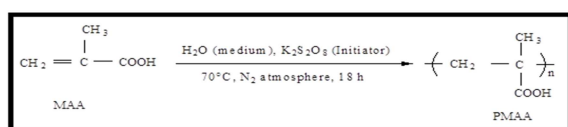
Equipments

Melting/molten temperatures of PMAU and urea were measured on a Gallenkamp apparatus without any correction. IR Spectrophotometer (Shimadzu,

FTIR-8900, Japan) and NMR Spectrometer (Bruker 400 MHz Ultra Shield™ NMR, Switzerland) were used for obtaining IR spectra (KBr) and ^1H NMR spectra (D_2O) respectively.

Preparation of Poly (methacrylic acid) [PMAA]

30 g of MAA was transferred to a three necked round bottom flask dipped in a water-bath at 70°C . The polymerization reaction was carried out in a nitrogen atmosphere in presence of 250 mL of water containing 0.6 g of KPS as initiator. The reaction was continued for 18 h with constant stirring. The polymerization of MAA is shown in Scheme 1.

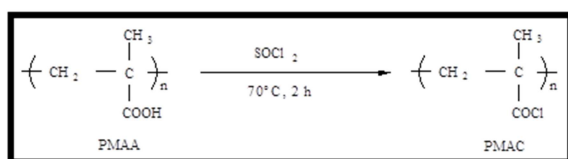


Scheme 1

Preparation of Poly (methacrylic chloride) [PMAC]

20 g of solid PMAA was taken into a three necked round bottomed flask and dissolved in water. 30 mL of thionyl chloride was added dropwise over 1 hour at low temperature ($5-6^\circ\text{C}$). After complete addition of thionyl chloride, temperature was raised to 70°C and continued heating for another 2 h.

The activated chlorinated product, PMAC was precipitated and dried at reduced temperature in a desiccators over anhydrous CaCl_2 . Chlorination of MAA is shown in Scheme 2.

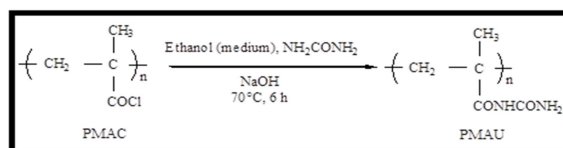


Scheme 2

Preparation of Poly (methacrylic urea) [PMAU]

5 g of solid purified PMAC was taken into a round bottom flask containing 300 mL of ethanol and was dissolved by heating. 30 g of urea and 0.5 g of NaOH were subsequently added. The content of the flask were heated under reflux at 70°C for 6 h. Finally PMAU was precipitated from ethanol and washed repeatedly with ethanol to remove any soluble urea or

impurities. The product was identified by elemental analysis, TLC measurement, FTIR and ^1H NMR spectra. Preparation of PMAU from urea is shown in Scheme 3.



Scheme 3

Soil preparation and fertilizer application

Plantation was carried out in earthen pot of 24 cm height and 30 cm diameter with a single hole at the center 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 super phosphate, 0.94g muriate of potash and 0.5 g gypsam. In each pot three green chili plants of 12-13 cm height (approximately 1 month old) were then planted. After 30 days of plantation, 1.07 g urea and 1.80g of PMAU were applied respectively in urea and PMAU treated pots, the quantities being estimated on the basis of percentage of nitrogen content (see 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 PMAU, urea and (without N-fertilizer) labeled as control. Plant height (ground level to the tip of flag leaf) number of leaves and leaf area were measured during plant growth from time to time. After de-plantation, total weight of dry-root, dry-stems and dry-leaves per plant were also measured. Nitrogen content in soils and plant parts were measured by the Kjeldahl method (AOAC). During cropping pots were maintained in open air with temperature and humidity.

Statistical analysis

The recorded data were analyzed statistically by using ANOVA technique following single factorial randomized complete block design. The differences among different treatments were evaluated by Duncan's New Multiple Range Test (DMRT). (The data were calculated with the help of SPSS package).

Results and discussion

The Fig.1 shows the FTIR spectra for urea and PMAU. In both the compounds broad absorption signal due to N-H stretching appeared between 3200-3600 cm^{-1} and a signal due to C=O appeared between 1600-1700

cm^{-1} . In PMAU two absorption signals due to N-H₂ and N-H bending appeared at 1463.9 and 1404.1 cm^{-1} respectively while in urea one such signal due to N-H₂ bending was observed.

Table1. Physical properties of PMAU and urea.

Properties	PMAU	Urea
Nature	Granular solid, brown color	Granular solid, white color
Solubility (g/100mL, at ambient temp.)	0.31	104
N content (%)	25.85	46.66
Molten temperature (°C)	105-110	120-125

The absorption band due to alkyl part of PMAU appeared in the range between 1153.4 and 1002.7 cm^{-1} . The ¹H NMR spectra of PMAU is shown in Fig. 2.

The chemical shifts due to amide (-CONH₂) and substituted amide (CONH) are observed at 5.69 ppm and 4.40 ppm respectively. In urea (Fig.3) only amide (-CONH₂) group is observed at 5.70 ppm. Chemical shift due to carboxyl group (-COOH) is not observed

in the spectra of PMAU in the region 10.5-12 ppm, indicating that carboxyl group has successfully been completely replaced by the substituted amide linkage. PMAU in solution presumably have complicated geometry due to the formation of hydrogen bond among inter and intermolecular chains making the correct assignment of all chemical shifts in PMAU spectra difficult.

Table 2. The analysis of variance (ANOVA) table for average plant height.

Source of variance (S.V.)	Degree of freedom (d.f.)	Sum of Square (S.S.)	Mean square (M.S.)	Variance ratio (F)
Treatments – T (PMAU, urea and control)	T-1 = 2	554.46	277.23	$F_1 = \frac{MS_1}{MS_3} = 15.68$
Block [column (r) wise]	r-1 9-1 = 8	4851.73	606.46	$F_2 = \frac{MS_2}{MS_3} = 34.87$
Error	(T-1)(r-1) 2×8 = 16	282.79	17.67	-
Total	N-1 = 27-1 = 26	5688.9800	-	-

N = Total number of experimental observations in three treatments.

Solubility is an important parameter that determine the performance of slow-release fertilizers (Dou and Alva, 1998) in agriculture. Solubility measurement that volume of water was necessary to dissolve PMAU as compared to urea (Table 1) and the

dissolution process was also comparatively slow, taken five 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 was obtained after five days. This slow dissolution and relatively low solubility of PMAU may be taken as an important prerequisite for being applicable as slow release fertilizer.

Table 4. N content in soil at 15 days interval.

Treatments (T) of soil	Duration, Days after transplantation, DAT					
	40 DAT (%)N/g	55 DAT (%)N/g	70 DAT (%)N/g	85 DAT (%)N/g	100 DAT (%)N/g	115 DAT (%)N/g
PMAU	0.3540	0.253	0.165	0.12	0.084	0.0584
Urea	0.2475	0.1175	0.056	0.03	0.016	0.01
Control (without N fertilizer)	0.068	0.046	0.034	0.024	0.015	0.01

Table 5. The analysis of variance (ANOVA) table for N content in soil .

Source of variance (S. V)	Degree of freedom (d.f)	Sum of Square (S.S)	Mean square (MS)	Variance ratio (F)
Treatments – T (PMAU, urea and control)	T-1 3-1 = 2	0.06051211	0.0302560	$F_1 = \frac{MS_1}{MS_3} = 13.98$
Block [column (r) wise]	r-1= 6-1=5	0.08336727	0.0166734	$F_2 = \frac{MS_2}{MS_3} = 7.707$
Error	(T-1) (r-1) 2×5 = 10	0.02163381	0.0021633	
Total	N-1 = 18-1 =17	0.16755127	-	-

N = Total number of experimental observations in three treatments.

Kjeldal method

Materials

Concentrated Sulfuric acid, Hydrochloric acid, Potassium sulfate, Merck, Germany, Merck Germany, Sodium hydroxide, BDH, England, Mercury (2) oxide, Merck Germany. And other chemicals were used.

Equipments

Long necked Kjeldal digestion flask, Distillation plant, Condenser, Burette, Pipette, Conical flask stand, and others glass ware were used.

Process description

About 0.5 g of sample was placed in a long necked Kjeldahl digestion flask. 0.7 g of mercury (II) oxide, 15 g of potassium sulphate and 40 mL of concentrated

H₂SO₄ were added, mixed thoroughly and the mixture was left to stand for 30 min. The mixture was heated for 1±25 hours at 390-410°C keeping the flask in an inclined position. After cooling the mixture 200 mL of water, 25 mL of 0.5M sodium thiosulphate solution and a few pieces of anti-bumping granules were added and mixed thoroughly. Sufficient amount of 11 M NaOH solution was then poured down the wall of the flask until the mixture turned strongly alkaline (approximately 120 mL). It is to be noted that before mixing the reagents, the flask was connected to a distillation apparatus in which the tip of the delivery tube was submerged just below the surface of a measured volume of HCl. The contents of the distillation flask were boiled until at least 150 mL of the liquid was distilled into the receiver. Methyl red

indicator was added to the HCl solution and titrate 0.1 M NaOH solution (titration a mL). Carry out a blank titration on the equal measured volume of the 0.1 M hydrochloric acid (titration b mL). The percentage of nitrogen in the sample is calculated by following equation.

$$\% \text{ N} = \frac{(b-a)0.1 \times 14 \times 100}{\text{weight of sample}} \quad (\text{Jeffery G.H. et al.})$$

Table 6. Mean difference table for N content in soil.

Mean of treatments	$t_1 = 0.17233$	$t_2 = 0.0795$	$t_3 = 0.03283$
t_3	0.139497**	0.0467	-
t_2	0.09283**	-	-
t_1	-	-	-

The average plant height in PMAU treated pot increased at a faster rate relative to that in the urea treated pot. In absence of N fertilizer (control) the plant height increased but relatively at a lower rate. The statistical analyses of the average plant height are

Fig. 4 shows the average plant height of chili plants measured after 50 days of transplantation at the interval of 10 days. Plant height increased with passing of time in PMAU, urea and control treated pots.

given in Table 2. The higher value of the observed F ratio relative to the corresponding tabulated one at the 5% level of significance implies a difference among the resultant plant heights with the variation in soil treatments.

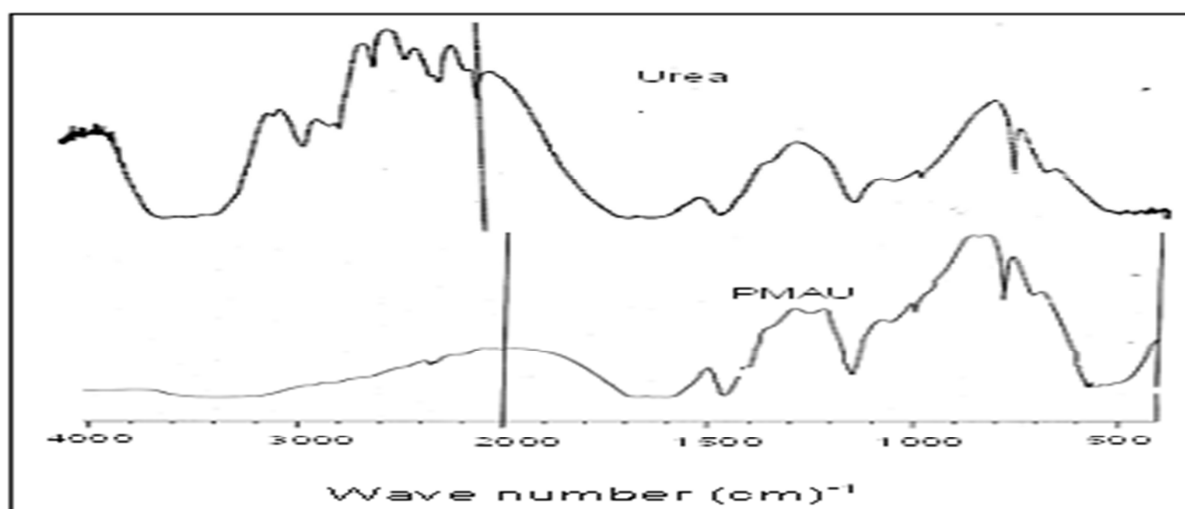


Fig. 1. FTIR for urea and PMAU.

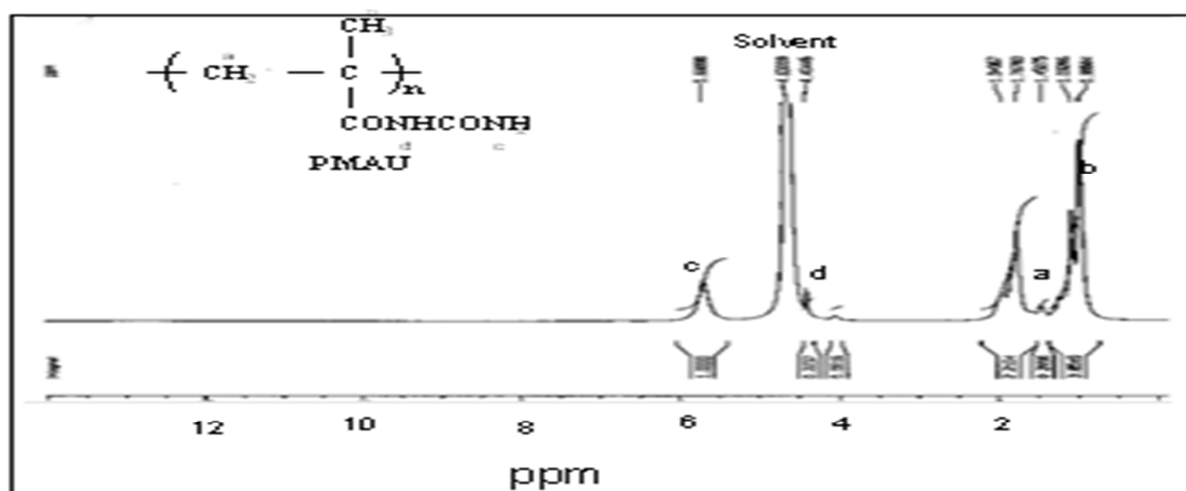


Fig. 2. ^1H NMR spectra of PMAU.

The mean difference values (Table 3) of both PMAU (11.09) and urea (5.97) from control are greater than the values of LSD at both 5% (4.25) and 1% (5.82) levels of significance. Moreover, the mean difference value in case of PMAU is higher than that of urea. These observations suggest that soil treated with PMAU gives a higher increase in the average height of

chili plant relative to those treated with urea and control. After 50 days of plantation leaves in each plant were counted in PMAU, urea, and control treated pots at 10 days of intervals during growth period. Figure. 5 shows the average number of leaves in each treated pot.

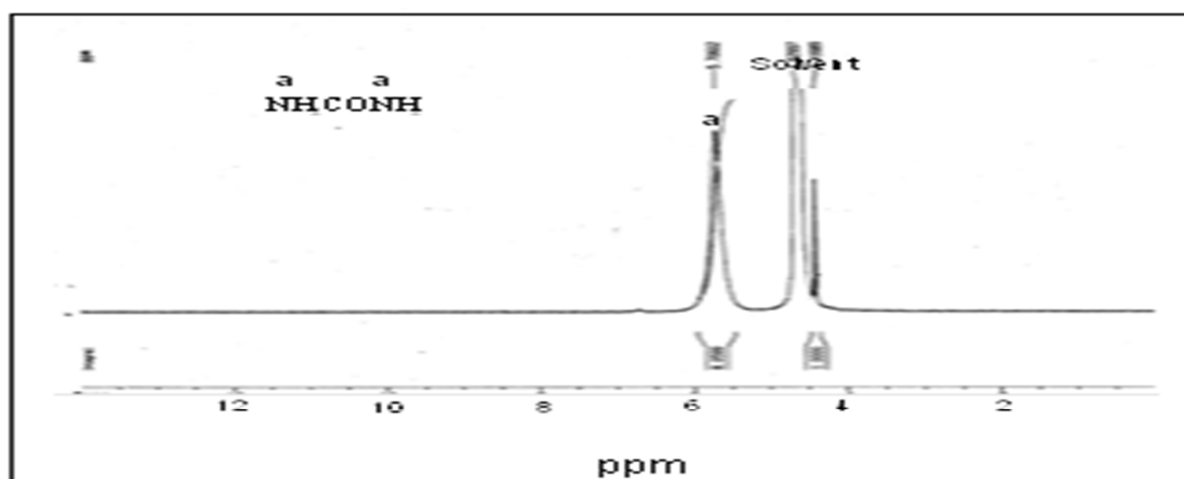


Fig.3. ¹H NMR spectra of Urea.

This figure also indicated that average number of PMAU treated plants leaves increased more rapidly than in urea and control treated pots. It may be mentioned that all the pots under experimental observation were subject to the same environment with controlled irrigation and rain water.

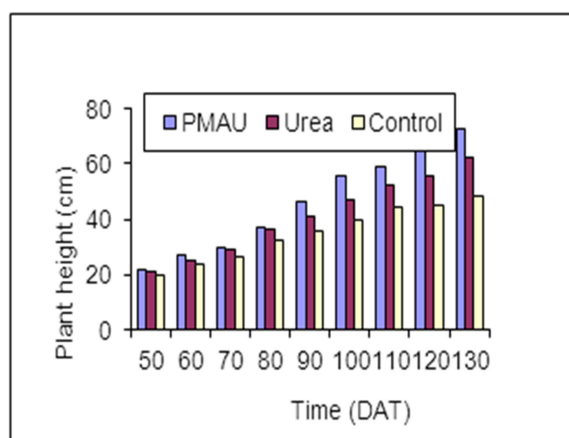


Fig. 4. Average plant height of chilli plants.

Therefore it can be assumed that the apparent increase in the growth of chilli plants in PMAU treated pot is due to the sustained and slow release of nitrogen. From the statistical analysis the mean difference value (20.11) of PMAU from control is

greater than LSD values at both 5% (5.15) and 1% (7.05) level of significance. Similarly the mean difference value (9.22) of PMAU from urea is also greater than LSD values at both 5% and 1% level of significance.

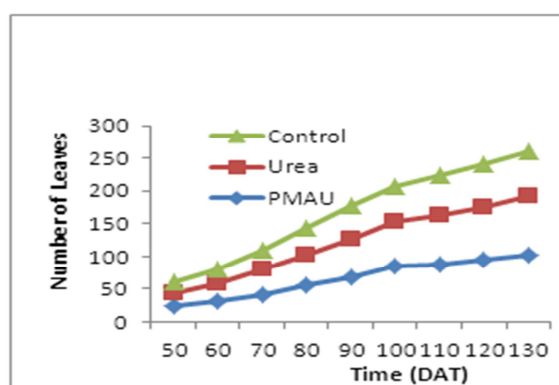


Fig. 5. Average number of leaves of chilli plants.

Therefore above analysis can be predicted that PMAU relatively increases the growth of plants.

$$\text{Least significant difference} = \left(\sqrt{2 \times S^2_{\bar{Y}}} \right) \times t_{16,5\%} = 4.25$$

$$\text{Least significant difference} = \left(\sqrt{2 \times S^2_{\bar{Y}}} \right) \times t_{16,1\%} = 5.82^{**}$$

In order to study the release behavior of nitrogen in soil, the nitrogen content in PMAU, urea and control treated soil were measured at various time intervals after plantation.

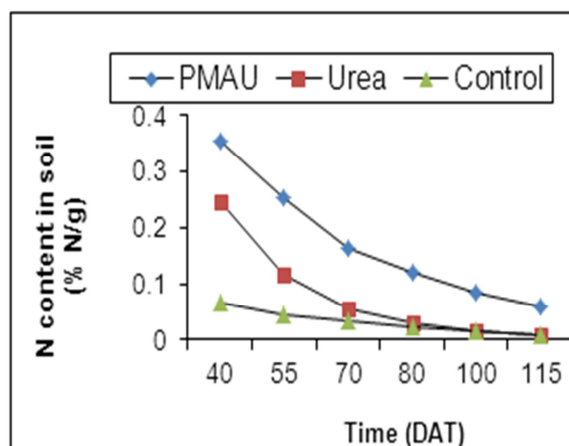


Fig. 6. N content in soils of chilli plants.

It may be mentioned that fertilizer were applied after 30 days of plantation and nitrogen level in the respective soil was measured after 10 days fertilizer application. Fig. 6 shows the variation of nitrogen content in PMAU, urea and control treated soils. Before transplantation the nitrogen content in the soil was 0.09%. Initially i. e after 10 days of fertilizer application PMAU treated soil has the highest nitrogen content followed by urea and control (Table 4.). 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 PMAU treated soil may be attributed to the combined effects of relatively low solubility, strong adhesion of macromolecular chain with porous soil particles and hence less vaporization and low leaching of the covalently bonded urea. Many researchers also reported improvement in growth and nitrogen uptake by seedlings using different types of slow release fertilizer (Krasowski *et al* 1999). However, it would be unwise to compare the value as uptake is always influenced by the pH, moisture and temperature etc. (Shaviv and Mikkelsen). In both urea and control treated soils, nitrogen content reduced rapidly and reached very low level in middle of cropping season while in PMAU treated soil nitrogen content reduced steadily. It is also observed that at end of cropping

season trace nitrogen is available in PMAU treated soil whereas in urea and control treated soils nitrogen content reduced almost zero.

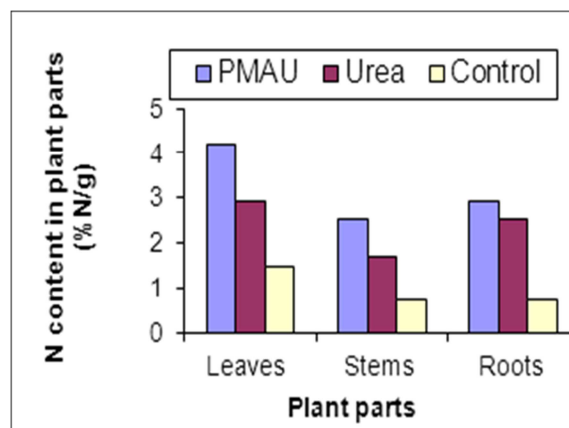


Fig. 7. N content in plant parts of chilli plants.

The optimum solubility of PMAU in water is important as it determines the availability of nitrogen for plant uptake. An important characteristic of all good controlled-release fertilizers is that most nutrients 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 PMAU 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 PMAU can be utilized as control-release nitrogen fertilizer. A statistical analysis (Table 5.) was also performed on the data of nitrogen content in soil obtained at different time interval during cropping. The mean difference value of PMAU (0.1394) from control is greater than LSD values at both 5% (0.059) and 1% (0.085) levels of significance but the mean difference value of urea (0.0466) from control is lower (Table 6.). Again the mean difference value of PMAU from urea (0.09) is higher than the LSD values at both 5% and 1% levels of significance.

$$\text{Least significant difference} = \left(\sqrt{2 \times S^2_{\bar{Y}}} \right) \times t_{10, 5\%} = 0.05983^*$$

$$\text{Least significant difference} = \left(\sqrt{2 \times S^2_{\bar{Y}}} \right) \times t_{10, 1\%} = 0.08509^{**}$$

Nitrogen level in plant parts such as stems, roots and leaves were also measured. It may be mentioned that stems, roots and leaves were collected after de-plantation end of cropping. Fig 7. shows the nitrogen level for plant parts obtained from three different treated soils. All of them PMAU treated soils plant parts content relatively higher nitrogen than from urea and control treated soils. This results suggests that the use of PMAU maximizes the uptake of nitrogen from the soil, because urea was bonded to polymer matrix which reduced the release of nitrogen. Therefore it is considered that PMAU has the potential to be used as controlled-release fertilizer.

Conclusion

PMAU, a slow-release fertilizer was prepared in three steps. In the first step MAA was polymerized in water medium using KPS as an initiator. In the 2nd step PMAA was activated by reacting with thionyl chloride. Finally the chlorinated derivative of PMAA was reacted with urea to give PMAU. The solubility of PMAU decreased 335fold as compared to urea. The effect of PMAU in agriculture was evaluated by studying the physical growth of green chilli plants and the obtained results showed that the growth of average plant size was better as compared to urea and control. The release behavior of nitrogen in soil and plant uptake was greatly improved in case of PMAU treated soil. These observations suggest that synthesized PMAU produced sustained and slow release of nitrogen during plantation and also minimized the loss of nitrogen through surface runoff, vaporization and leaching.

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