RESEARCH ARTICLE

ROLE OF SLOW RELEASE POLYMER COMPOSITE FERTILIZER ON NITROGEN AVAILABILITY IN SOIL

*Rahman, M .H.*

Department of Crop Science and Technology, University of Rajshahi, Rajshahi 6205, Bangladesh

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ABSTRACT

Agriculture is considered as a big industry in a sense that huge man power and money are involved. The farmers are always trying to get high production with minimum cost. It is well known that fertilizer is one of the major factors of crop production and nitrogen is essential macronutrients required by the plants for their growth, development and yield. The most widely used nitrogen containing fertilizer is urea because high content of nitrogen (46\%N) commercially available and low cost of production. However high solubility followed by overdose in application causes economic loss and ecological imbalance. In this regard designing of a slow or controlled release technology which increased the efficiency use of urea fertilizer as well as checking environmental pollution. In this research our main objective is to reduce solubility by the fixing urea to biodegradable polymer matrix. In this work a copolymer were used. Acrylamide (AAm) and Maleic acid(MA) were used for this purpose. This was prepared by solution copolymerization of acrylamide and maleic acid and urea was then covalently fixed through the activated carboxylic groups. The resulting product name is \( \text{P(AAm-MA)} \text{U} \). A pot experiment was carried out to investigate the effect of \( \text{P(AAm-MA)} \text{U} \) in soil by studying on the physical growth of green chilli “capsicum annum” plants. The examined result showed that all growth characteristics parameter namely plant height, number of leaves, leaf weight and area, nitrogen in leaf and in soil during cropping season were higher when pots were fertilized with copolymer matrix as compared to urea and control (without N-fertilizer). Results also showed that fresh weight of leaves, roots, stems, total dry matter and nitrogen in plant parts and in soil after de-plantation were grater than that of urea and control. The nitrogen release behavior in soil over the cultivation period and plant uptake of nitrogen suggested that \( \text{P(AAm-MA)} \text{U} \) can be used as slow release nitrogen fertilizer.

\textbf{Key words:} Slow release, N-fertilizer, \( \text{P(AAm-MA)} \text{U} \), Fixation, Matrix, Solubility, Uptake.


INTRODUCTION

The demand for food by the growing world population would require huge agriculture output and hence more intensive agricultural crop production. Several recent studies have suggested that the expected continual yield and production increments are likely to require increased application of fertilizer (Peltonen and GrowHow, 2003). In developing countries like Bangladesh, a projected increase in fertilizer use will occur as food productions need to be urgently (Guo \textit{et al.}, 2005). So there is a positive correlation observed between plant production and fertilizer used. Broadly speaking a fertilizer is any material, organic or inorganic, natural synthetic that furnishes to plants one or more of the chemical elements necessary for normal growth (Hignet). Nitrogen fertilizer plays a major role in achieving maximum crop yield in agriculture and nitrogen is a macro nutrient essential for plant growth and development. Among the nitrogen fertilizers, the most widely used one is urea because of its high nitrogen content (46\% N) and comparatively low cost of production (Liu \textit{et al.}, 2006).

However due to surface runoff, leaching and vaporization, the utilization efficiency or plant uptake of urea generally reduced to below 50\% (Abraham and V.N.R Pillai 1996). The loss of urea could cause very serious environment problems. Other important nitrogen containing fertilizers are ammonium nitrate (33.5\% N), ammonium sulfate (20.21\% N). These fertilizers are highly soluble in water and easily washed away in different ways resulting in huge economical losses. Nitrogen loss after application to the soil caused non-uniform release of nitrogen to the plant during growth stage. For this reason due to low nutrient reserves lower amount of fertilizer is required for optimum plant growth. The loss of nitrogen from soil may occur in several ways. A few are outlined here.

\textbf{Leaching or surface drainage:} Heavy rains or poorly controlled irrigation may leach the nitrogen beyond the reach of plant roots or carry it away in surface drainage. In either case the nitrogen is lost from the cropland and may contaminate streams, lakes or underground water supplies [(Hignet T.P*)].

\textbf{Volatilization as ammonia:} Surface applied urea rapidly hydrolyzes to ammonia and carbon dioxide. Part of ammonia may be volatilized into the atmosphere. Also ammonia may be
volatilized the ammonia dissolved in the surface water may be volatilized (Hignet T.P*).

Decomposition: Under anaerobic conditions (flooded or water logged soils) nitrates are reduced to nitrites, which are unstable and decompose forming elemental nitrogen or nitrogen oxide that escapes to the atmosphere (denitrification). Ammonia nitrogen is rapidly oxidized to nitrate under aerobic soil conditions and may subsequently be lost by denitrification when it leaches into the anaerobic sub soil layer or when the soil becomes water logged or flooded.

Nitrogen is lost from most soils in several steps [(Hignet T.P*)].

\[ \text{NO}_3^- \rightarrow \text{HNO}_2 \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]

Last 3 compounds can escape to the atmosphere as a gas. To overcome the nitrogen loss farmers often use excess nitrogen fertilizer. Excessive use of nitrogen containing fertilizer in land leads to accumulation of nitrate into the soil which are transferred to man through plants. Nitrates being highly soluble, go into drinking ground water and become toxic when this concentration exceeds 90 ppm, causing diarrhoea and cyanosis (Blue Jaedice) in children. In human body these nitrates and nitrites are converted to nitrosoamines and nitroso compounds which are suspected as agents of stomach cancer (Sharma B.K.). Considering the above situation, one method to effectively reduce nutrient losses in the use of slow or controlled release fertilizer. In general slow or controlled release fertilizers demonstrate many advantages over the traditional type, these are decreased rate of losses of fertilizer from the soil by rain or irrigation water, sustained supply of nutrient for a prolonged time, increased utilization efficiency of fertilizer, lowered frequency of application, minimized potential negative effects associated with over dosage and reduced toxicity (Tomaszewksa and Jarosiewicz. 2002). The philosophy of slow and controlled release fertilizers has been accepted well and many have the opinion that these fertilizers would have high market potential for arable and forage crops.

Controlled release fertilizers are coated and slow release fertilizers have a chemically reduced or low solubility (Trenkel 1997), the latter being mainly derivatives of urea. In both groups the actual nitrogen release and solubility are on purpose low because they need to provide a controlled release of plant nutrients adapted to the demand of the crop and for minimizing the risk for losses. Slow release nitrogen containing fertilizer that for any reason release its nitrogen content over an extended period. There are many reports dealings with the preparation and properties of slow and controlled release fertilizers, which are widely used in agriculture. The urea-formaldehyde fertilizer, which is a representative controlled-release nitrogen fertilizer, is synthesized from urea and formaldehyde in the presence of a catalyst at various temperature conditions (Alexander and Helim 1990). The urea-formaldehyde fertilizer is degraded by soil microorganisms, resulting in the gradual release of urea into the soil, which is then further metabolized by soil microorganisms into plant available nitrogen forms such as ammonium and nitrate (Thomas et al., 2003). Researchers studied the effect of several slow-release fertilizers on decreasing ammonia volatilization and N leaching. The results indicated that the development of CRF is a green technology that not only reduces nitrogen loss caused by volatilization and leaching but also alters the kinetics of nitrogen release (Du et al., 2007). The studied slow-release fertilizer encapsulated by graphene oxide films, and the results showed that new coating technology could hold great promise for the development of environmentally benign controlled-release fertilizer for crop production (Zhang, et al., 2014). A report was found that polygorskite-coated fertilizer could be promising for potato production and be beneficial to agricultural sustainability in semi-arid areas (Song et al., 2014). A experiment gave some insight to design and characterize new versatile organogelators and soft coated materials with special molecular structures (Guo et al., 2014 and Jiao et al., 2011). A double-coated slow-release NPK compound fertilizer was prepared and the results showed that this product with excellent slow release and water-retention capacity, being nontoxic in soil and environment-friendly, could be especially useful in agricultural and horticultural applications (Wu and Liu, 2008). A report was found that slow-release N fertilizers are not an alternative to urea for fertilisation of autumn-grown tall grass (Rodrigues et al., 2010). A experiment was contacted with a novel slow-release NPK fertilizer encapsulated by superabsorbent nanocomposite. The results indicated that the presence of the montmorillonite caused the system to liberate the nutrient in a more controlled manner than that with the neat superabsorbent. The good slow-release fertilizer property as well as good water retention capacity showed that this formulation is potentially viable for application in agriculture as a fertilizer carrier vehicle (Rashidzadeh and Olad 2014). In this research our main objective to reduced the loss nitrogen by covalently binding highly water soluble urea to a biodegradable polymer matrix that would permit ultimately the slow release plant nutrient nitrogen. The polymer matrix would limit the solubility of nitrogen in water and thereby would maintain the appropriate concentration in soil for long time. A copolymer matrix, P(AAm-MA), comprising acrylamide (AAm) and maleic acid (MA), was used for the covalent fixation of urea. The product covalently bonded urea polymer composite P(AAm-MA)U was characterized by FTIR, 1 H NMR, TLC measurement and elemental analysis. Here AAm is a nitrogen containing monomer and MA is a dibasic acid. The purpose of selecting these monomers was to increase the N content in the fertilizer product. In the application phase, relative growth responses of green chilli ‘Capsicum annuum’ plants were studied in presence of P(AAm-MA)U, urea and control (without N fertilizer) respectively. The release behavior and plant uptake of nitrogen were also measured during cropping.

MATERIALS AND METHODS

MA and AAm of monomer grade, from( LOBA, Chemika, India) was distilled under reduced pressure and preserved in the refrigerator. Potassiumpersulfate (KPS) of reagent grade from LOBA, Chemica, India, was recrystallized from water at low temperature and preserved in the refrigerator. Thionyl Chloride from BDH, England and urea [NH2CONH2] as N fertilizer were of commercial grade. NaOH, H2SO4, Na2S all of reagents grade were used without further purification. Distilled deionized water 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
Preparation of chlorinated product of \( \text{P(AAm-MA)} \): 40 g of dried \( \text{P(AAm-MA)} \) was taken into a three necked round bottom flask and dissolved in water. Then 50 mL of thionyl chloride was added drop-wise over 1 h at low temperature (5-6°C). After the addition of thionyl chloride temperature was raised to 70°C and heating continued for another 2 h. The activated \( \text{P(AAm-MA)} \) was obtained and the volume of the reaction mixture was reduced simply by heating. The reaction is shown in Scheme 2.

Application of \( \text{P(AAm-MA)} \) in soil

Plot selection and soil preparation: \( \text{P(AAm-MA)} \) was applied in soil to see the growth of green chilli \( \text{Capsicum annum} \) plants. A comparative study with urea and control (without N fertilizer) was carried out under identical conditions. Four pots for the treatment of each \( \text{P(AAm-MA)} \), urea and control were used. Before plantation experimental details in Table 1.

FTIR spectra for urea and \( \text{P(AAm-MA)} \) are shown in Figure 1. In both compounds broad absorption band due to N-H stretching is observed between 3200-3500 cm\(^{-1}\) and a band due to C=O is appeared between 1600-1700 cm\(^{-1}\). \( \text{P(AAm-MA)} \) gave two absorption signals due to N-H and N-H bending at 1406.00 and 1274.90-1325 cm\(^{-1}\) respectively while in urea one such signal due to N-H bending is observed. This is as indication that urea has been fixed to the copolymer matrix. The absorption band due to the alkyl part of \( \text{P(AAm-MA)} \) appeared in the range between 1008.7-1213.1 cm\(^{-1}\). The \( ^1 \)H NMR spectra for \( \text{P(AAm-MA)} \) is shown in Figure 2. The chemical shifts due to amide group is observed at 8.93 ppm and 5.64 ppm respectively. In urea (see Fig. 3) the chemical shift due to only amide group (CONH\(_2\)) is observed at 5.70 ppm. The absence of any chemical shift due to carboxyl group (COOH) in the modified polymer matrix is completely eliminated by the substituted amide linkage due to the formation of covalent bond with urea. It was not possible to assign all the chemical shifts appeared in the NMR spectra of \( \text{P(AAm-MA)} \), because macromolecules in solution is expected to have complicated chemical structure resulting from hydrogen bonding among inter or intra molecular chains.

In TLC measurements, both urea and \( \text{P(AAm-MA)} \) gave sharp single spots with different \( R_f \) values of 0.918 and 0.824 for urea and \( \text{P(AAm-MA)} \) respectively. This indicates that new compound has been formed due to the fixation of urea with activated copolymer matrix. The N content in \( \text{P(AAm-MA)} \) measured by the Kjeldahl method was found 32.85%. Since it is a random copolymer having complicated chemical structure the theoretical N content could not be predicted. However, the above elemental and spectral analyses suggest that urea is bonded to the copolymer matrix. Solubility is an important parameter that determine the performance of a slow-release fertilizer (Dou and Alva, 1998). Solubility measurement indicates that large volume of water is necessary to dissolve copolymer matrix \( \text{P(AAm-MA)} \) (Table 2) and the dissolution process was also relatively slow, taken four days. The first stage in copolymer dissolution was characterized by swelling due to the slow penetration of the water molecules into the interstices of the copolymer matrix.
Figure 1. FTIR for urea and P (AAm-MA)U

Figure 2. $^1$H NMR for P(AAm-MA)

Figure 3. $^1$H NMR for Urea

Table 1.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earthen pot with single hole</td>
<td>24cm height, 30 cm diameter</td>
</tr>
<tr>
<td>Total area of each pot</td>
<td>0.07 m$^2$</td>
</tr>
<tr>
<td>Soil for each pot</td>
<td>12kg, sandy loam texture, pH 7.9</td>
</tr>
<tr>
<td>Triple super phosphate TSP</td>
<td>1.52g</td>
</tr>
<tr>
<td>Muriate of potash (MP)</td>
<td>0.94g</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.50g</td>
</tr>
</tbody>
</table>
Figure 4. Average height of chilli plants

Figure 5. Average number of leaves of chilli plants

Figure 6. Leaf area of chilli plants

Figure 7. Nitrogen content in leaves

Figure 8. Nitrogen content in soils

Figure 9. Nitrogen in plant parts

Table 2. Physical properties of P(AAm-MA)U and urea.

<table>
<thead>
<tr>
<th>Properties</th>
<th>P(AAm-MA)U</th>
<th>Urea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature</td>
<td>Sticky solid, white color</td>
<td>Granular solid, white color</td>
</tr>
<tr>
<td>Solubility (g/100mL, at ambient temp.)</td>
<td>0.35</td>
<td>104</td>
</tr>
<tr>
<td>N content (%)</td>
<td>32.85</td>
<td>46.66</td>
</tr>
<tr>
<td>Molten temperature (°C)</td>
<td>190-195</td>
<td>120-125</td>
</tr>
</tbody>
</table>
As swelling continued more and more segments of the copolymer molecules were solvated and loosened out. The loosened copolymer P(AAm-MA)U molecules then diffused slowly out of the copolymer matrix and dispersed in the water phase resulted in a completely homogeneous solution after four days. This slow dissolution and relatively low solubility of copolymer P(AAm-MA)U may be taken as an important prerequisite for being applicable as a slow release fertilizer. Figure 4, shows the average plant height of chili plants in each copolymer matrix, urea and control treated pots. The plant height was measured after 50 days of transplantation at an interval of 10 days. In all cases the plant height increased with passing of time.

However in P(AAm-MA)U treated pot the average plant height increased at a faster rate after 80 days of plantation (i.e., after 50 days of fertilization) as compared to that in the urea treated pot. In absence of urea (control) the plant height increased but relatively at a lower rate. The observed F ratio is greater than the tabulated value at 5% level of significance. This implies a significant difference among the plant heights with the variation of soil treatments. The mean difference values (Table 3) of both P(AAm-MA)U (10.17) and urea (6.03) from control are greater than the values of least significant difference (LSD) at both 5% (3.88) and 1% (5.38) level of significance. The mean difference value in case of P(AAm-MA)U is comparatively higher than that of urea. Hence P(AAm-MA)U offered a larger plant height relative to urea. The average number of leaves were also measured at different time intervals per chilli plants in P(AAm-MA)U, 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 that is in copolymer matrix P(AAm-MA)U treated pots the average number of leaves increased more rapidly than in urea treated pots. It may be mentioned that all the pots under experiment were subjected to the same environment with controlled irrigation and rain water.

| Table 3. Mean difference table for average plant height. |
| t1 = 45.26 | t2 = 41.12 | t3 = 35.09 |
| t1 | 10.17** | 6.03** | - |
| t2 | 4.14* | - | - |
| t3 | - | - | - |

Least significant difference (LSD) = \( \sqrt{2 \times S^2 \times t_{(a, n-1)}} \) where n = 38, for P(AAm-MA)U at both 5% (3.88) and 1% (5.38) level of significance.

| Table 4. Mean difference table for average number of leaves per plant |
| t1 = 62.44 | t2 = 56.22 | t3 = 45.33 |
| t1 | 17.11** | 10.89** | - |
| t2 | 6.24** | - | - |
| t3 | - | - | - |

Least significant difference (LSD) = \( \sqrt{2 \times S^2 \times t_{(a, n-1)}} \) where n = 38, for P(AAm-MA)U at both 5% (3.88) and 1% (5.38) level of significance.

| Table 5. Mean difference table for N content in soil |
| t1 = 0.1735 | t2 = 0.0795 | t3 = 0.03283 |
| t1 | 0.1407** | 0.0467 | - |
| t2 | 0.094** | - | - |
| t3 | - | - | - |

Least significant difference (LSD) = \( \sqrt{2 \times S^2 \times t_{(a, n-1)}} \) where n = 38, for P(AAm-MA)U at both 5% (3.88) and 1% (5.38) level of significance.

There it can be assumed that the apparent increase in growth of chilli plants in copolymer matrix P(AAm-MA)U treated pots are due to the sustained and slow release of nitrogen from the copolymer matrix. The observed F ratio is greater than that of tabulated one. The mean difference values of P(AAm-MA)U (17.11) and urea (10.89) from control are greater than LSD values at both urea 5% (4.57) and 1% (6.23) level of significance (Table 4). Moreover the mean difference value of P(AAm-MA)U from urea (6.24) is greater than LSD values at both 5% and 1% level of significance. Hence P(AAm-MA)U offered a relatively faster growth of plants. The average leaf area of the plants was measured by graphical method at different time intervals during cropping season. The leaf area is an important parameter that is influenced by nutrient level in soil. The measurements started after 80 days of plantation i.e. after 50 days of fertilizer application. In all cases the leaf area remained almost steady with time but in P(AAm-MA)U treated pot the leaf area increased rapidly with cropping time as compared to urea and control.

This variation of leaf area is shown in Figure 6. Since the leaf area is determined by the level of nutrient available from the soil, the average leaf area in absence of N fertilizer was much lower than that with urea and P(AAm-MA)U treatments. Comparatively in P(AAm-MA)U treated pot the leaf area showed the highest value. The statistical analysis shows significant difference among three treatments. Both values of F ratio are greater than those of tabulated values. The mean difference values of P(AAm-MA)U (59.32) and urea (48.70) from control are greater than those of LSD values at 5% (2.52) and 1% (3.68) level of significance. Statistical analysis indicates that application of P(AAm-MA)U increased the effect on leaf area as compared to urea and control. Figure 8: Nitrogen content in soils Figure 9: Nitrogen in plant parts In order to study the release behavior of nitrogen in soils, the nitrogen content in P(AAm-MA)U, 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 respective soil was determined after 10 days fertilizer application. Figure 8 shows the variation of nitrogen content in P(AAm-MA)U, urea and control treated soils.

Before plantation the N content in the soil was 0.09%. Initially i.e. after 10 days of fertilizer application P(AAm-MA)U treated soil has the highest N content followed by urea and control. Relatively the low nitrogen level in urea treated soils is expected to be due to the surface runoff, evaporation and leaching (Abraham and Pillal, 1996). However the initially higher nitrogen content in P(AAm-MA)U treated soil is derived from the combined effects of relatively low solubility, strong adhesion of macromolecular chain with porous particles and hence less vaporization and poor leaching of the covalently bonded urea. Many researchers also reported improvement in growth and nitrogen uptake by seedling 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 urea and control treated soils, nitrogen content reduced rapidly very low level in the middle of the cropping season while in copolymer matrix treated soil nitrogen content reduced steadily. It is also observed that at the end of cropping season trace (0.06%) nitrogen is available in copolymer matrix treated soil whereas in urea and control treated soil nitrogen content...
reduced almost zero. The optimum solubility of copolymer matrix 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; Oretli, 1980). The decreasing tendency and ultimate value of nitrogen in copolymer matrix treated soil showed that only trace nitrogen is available for the next crop and this almost equivalent to the nitrogen content before plantation (0.09%). This behavior suggests that copolymer matrix 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 (Table 5 ) of P(AAm-
MA)U (0.1407) from control is greater than LSD values at both 5% (0.057) and 1% (0.081) level of significance. Again the mean difference value of P(AAm-MA)U from urea (0.094) is higher than LSD values at both 5% and 1% level of significance. Hence this analysis also indicates that in case of P(AAm-MA)U, N availability in soil is higher than in urea and control treated pot.

Nitrogen level in stems, roots and leaves of plants were also measured by Kjeldal method(AOAC). It may be mentioned that stems, roots and leaves were collected after de-plantation at the end of cropping. Figure 5 shows the nitrogen level for plant parts obtained from three different treated soils. The nitrogen content in all three plant parts obtained from P(AAm-MA)U treated soil shows relatively higher value. This result suggests that the use of P(AAm-MA)U maximizes the uptake of nitrogen from soil. So P(AAm-MA)U can be considered to release nitrogen at a rate slower than urea. Above observation again suggests that the use of urea of bonded to copolymer matrix reduced the release of nitrogen and hence the loss of nitrogen through leaching, volatilization and irrigation water.

Conclusion

P(AAm-MA)U was synthesized in three steps. P(AAm-MA) a kind of random copolymer was first prepared by solution copolymerization of AA and MA in presence of KPS initiator. Carboxyl groups in the polymer matrix were activated by chlorination and then reacted with urea. The product was characterized by TLC measurements, elemental and spectral analyses. The performance of P(AAm-MA)U in agriculture was followed by studying the growth of green chilli plants and compared the results with urea and control (without N-fertilizer) under identical condition. Comparative release behavior of nitrogen was also studied by measuring the nitrogen level in soil during plant growth. The results suggest that P(AAm-MA)U improved the growth of plants as well as sustained a higher nitrogen level in soil for longer time.

REFERENCES


