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CONTROLLED SLOW RELEASE OF UREA FERTILISERS FROM POLYMER MATRICES

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1. Introduction

Nitrogen is one among the three major nutrients required by plants. The most widely used N-fertilizer is urea due to its low cost of production and high N content (46%). The use of gh doses of high analysis fertilizer is very important for velopment. The consumption of fertilizers has been increasing enormously for the last several years. However studies all over the world have shown that conventional use of high doses of N- fertilizers will result in high losses and urea is no exception. Food and Agricultural Organisation (FAO) of United Nations has estimated that 40-70% of the fertilizer applied is lost (C. Hepburn and R. Arizal, 1988). Efficiency of urea in soil is generally less than 50% (Trivedi and Pachayiapan, 1979). In India about 85% of total N-fertilizer produced is urea and due to the heavy rain, hot climate and the method of application, (surface broad-casting) the loss of urea is very high. The urea loss is mainly by ammonia volatalization, denitrification, leaching and run off into water as nitrate. The portion of applied N, remaining unabsorbed by plants cause very serious environment problems. One of the deleterious effects of oxides of nitrogen (evolved out of applied urea) is the destruction of the ozone layer (Gopakumar et al. 1993). The unused nitrate ions from the agricultural fields, by run off nd leaching, finally enters the canals and lakes or groundwa r creating hazardous health problems. If the concentration of nitrate exceeds 11.3mg/1r in drinking water it can cause 'methaemoglobinaemia' in babies and cancer in adults (C. Hepburn et al, 1987). Many European countries have already taken steps to alleviate this 'Chemical time bomb' as often called by water scientists. One of the suggestions to overcome this problem was to eliminate or minimize the use of N-fertilizers. This would drastically reduce the crop-yield. Hence it is highly necessary to investigate strategies which increase the efficiency of N-fertilizers especially urea.

One of the methods to improve urea efficiency is to encapsulate it with suitable inert materials. Controlled Release Technology (CRT) is highly useful in this regard. The Scientific Advisory Committee to Prime Minister of India in their report in 1988 says "Much of the urea applied to soil is lost due to leaching and nitrification. Controlled Release of Urea could offer impressive savings, but we have not provided sufficient S&T inputs in this vital area to make this possible". FAO suggested that the fertilizer manufactures may improve the fertilizer efficiency by developing Controlled Release Fertilizers. Moreover OECD in its report about water pollution suggested to continue research in Controlled Release Fertilizers (C. Hepburn et al, 1987).

Controlled Release fertilizers have several advantages over the conventional fertilizers. Because of the sustained release of nutrients in a regulated manner for a longer time, mineral deficiencies can be corrected. Moreover, application frequency can be reduced. Considerable reduction in volatalization and leaching losses can be achieved by the use of controlled release fertilizers and thereby pollution can be minimized. Salt injury to young seedlings can be very well controlled by the use of such fertilizers (Joyce et al. 1988).

Acrylate polymers like poly methyl methacrylate and its copolymers are very widely used as soil conditioners to improve chemical, physical, bacteriological and agronomical properties of soil. Besides, these materials can reclamate alkaline and saline soils. (Azzam, 1980). The use of divinyl benzene (DVB) cross linked polymethyl methacrylate as a polymer matrix to encapsulate urea fertilizer is described in this paper. The laboratory level preparation and evaluation of the slow release behaviour of the products are investigated.

2. Experimental

(A) Preparation of DVB crosslinked PMMA - Polymer Coated Urea (PCU)

Polymethyl methacrylate crosslinked with divinyl benzene was used for coating urea. Thermocoal (TC), Natural Rubber (NR), ethyl vinyl acetate (EVA) and poly vinyl chloride (PVC) were used as sealants for coating.

Polymerisation was carried out by free radical solution method in chloroform and the initiators were azobis isobutyronitrile (AIBN) and tetramethyl ethylene diamine (TEMED). Fertilizer grade urea granules (25g) were suspended in chloroform (20ml) containing methyl methacrylate (2.54ml), DVB (0.3ml) and AIBN (0.1g). While stirring, the temperature was raised to 40°C using a water bath and the initiator TEMED (0.05ml) added. As the medium became viscous sealant (1g, TC/NR/EVA or PVC) and wax (1g) dissolved in chloroform were added. Heating and stirring were continued for one hour, and the solvent was evaporated. The product polymer coated urea was dried in an ovean at 70°C. The dried product was recoated using same amount of monomers and sealants by the same procedure.

(B) Evaluation of Polymer Coated Ureas

Polymer coated ureas were evaluated using water release, leaching and incubation studies. The PUC samples (2g) were suspended in preboiled distilled water (100ml) for different periods of time. The amount of urea released into the water was estimated (Watt and Crisp, 1954) after separating out the PCU granules. All the experiments were done in triplicate. In leaching studies PCU were applied (200 mg N/kg soil) to soil (1kg, 2mm sieved) in a PVC cylinder of 90mm diameter. The soil was pre-equilibrated by passing 0.1 N $CaCl_2$ solution through it, for 3 days. The soil samples containing PCU were leached using 0.1N $CaCl_2$ solution (100ml) at different intervals of time (1st, 2nd, 7th, 14th, 21st, 28th and 45th days). The leachate was analysed for NH_4-N (Kjeldahl's method) and Urea-N (Watt and Crisp, 1954). A control and blank experiments, viz. with uncoated urea and no fertilizer respectively were also carried out. In incubation study among the 4 PCU systems, two better performed from leaching studies viz. 'TC' and 'NR' systems were selected. PCU (20mg) was well mixed with soil (100g) and kept in a plastic beaker for different periods of time. Water holding capacity (WHC) of the soil was determined and 50% WHC was maintained throughout the experiment. A control experiment was also done. Soil samples after incubation periods (2, 7, 14, 21 and 28 days) were extracted using 0.1 N $CaCl_2$ solution and NH_4-N and urea N were estimated. All the experiments were carried out in triplicate and the results were analysed using a 2 factorial CRD design.

3. Results and Discussion

Time taken for complete release of urea in water and weight per cent of coating materials are given in table 1.

Table 1. Water release of Polymer Coated Ureas

PCU	Release time (hrs)	Weight of Coating Materials (%)
TC	15	16.8
NR	9	13.3
EVA	7	17.3
PVC	6	10.0

Water release pattern indicates that the sealants 'TC' and 'NR' are better than 'EVA' and 'PVC'. Leaching experiments clearly indicate the advantage of coating systems over control (Table 2 and Table 3). All PCU systems were found to be performing better than the control. From uncoated urea 84.2% of total N (NH_4-N + Urea N) was leached out by 2nd day, while only 21.6, 40.8, 45.7 and 44.5 total N (%) leached out from TC, NR, EVA and PVC systems respectively. At the end of the experiment the cumulative total N(%) leached were 92.3, 72.8, 81.1, 84.6 and 90.3 from control, TC, NR, EVA and PVC systems respectively. This clearly indicates the slow release behaviour of the PCU systems. In leaching studies the better performed slow release systems were 'TC' and 'NR' and they were selected for incubation study. NH_4-N and Urea N estimated at different experimental time in the incubation study are shown in Table 4 and Table 5 respectively.

Table 2. Total Nitrogen (mg) leached at different time intervals

Systems Time (Days)	TC	NR	EVA	PVC	Control	Average
1	17.5	40.0	47.8	43.0	84.8	46.6
2	25.9	41.8	43.6	46.1	83.8	48.2
7	40.4	43.3	47.8	48.5	11.0	38.2
14	27.2	20.5	14.4	22.3	2.5	17.4
21	18.7	8.7	7.5	14.1	1.5	10.1
28	10.0	4.6	5.1	2.6	0.7	4.6
45	6.0	3.6	3.0	4.2	0.3	3.4
Average	20.8	23.1	24.2	25.8	26.4	

Critical Difference, Time 0.6
Systems 0.5
Time X Systems 1.32

Table 3. Cumulative total nitrogen (mg) leached at different time intervals

Systems Time (Days)	TC	NR	EVA	PVC	Control	Average
1	17.5	40.0	47.8	43.0	84.8	46.6
2	43.3	81.7	91.4	89.1	168.5	94.8
7	83.7	125.0	139.2	137.6	179.5	132.9
14	111.0	145.5	153.6	159.8	182.0	150.4
21	129.7	154.1	161.1	174.0	183.5	160.5
28	139.7	158.7	166.2	176.5	184.2	165.1
45	145.7	162.3	169.2	180.7	184.6	168.5
Average	95.8	123.9	132.7	137.2	166.7	

Critical Difference Time 1.5
Systems 1.3
Time X Systems 3.4

Table 4. NH_4-N at different time intervals of Incubation study

Systems Time (Days)	TC	NR	Control	Average
2	5.6	6.4	13.95	8.5
7	6.0	9.4	19.1	11.5
14	8.0	10.8	19.4	12.7
21	11.0	12.1	19.2	14.1
28	13.1	15.2	19.1	15.8
Average	8.6	10.8	18.1	

Critical Difference Time 0.31
System 0.24 Time X Systems 0.53

Table 5. Urea-N at different time intervals of incubation study

Systems Time (Days)	TC	NR	Control	Average
2	14.2	13.0	5.2	10.8
7	13.2	10.1	0.0	7.8
14	11.4	8.3	0.0	6.6
21	8.0	7.2	0.0	5.1
28	6.1	3.9	0.0	3.3
Average	10.6	8.5	1.0	

Critical Difference Time 0.20
Systems 0.16
Time X systems 0.35

A significantly lower amount of NH_4-N was present in the soil with TC and NR systems than that with control, throughout the experiment. Similarly a significantly higher amount of urea N in soil with PCU were observed than control. No detectable level of urea was present in the control soil by 7th day of the study, which is due to the microbial conversion of urea to ammonical form. In the case of PCU systems the level of urea-N was gradually decreased as a function of time, suggesting a time - dependant release pattern. The amount of released urea is significantly higher for 'NR' system than for 'TC' system. At the end of the experiment per cent Urea-N remained were 30.5 and 19.5 for TC and NR systems respectively.

4. Conclusion

Urea can be incorporated in polymer matrices without inhibiting the polymerization process of MMA and DVB. The copolymers of MMA and DVB can be used as an efficient matrix system for urea fertilizer to impart slow release character. Expanded polystyrene (thermocoal) used extensively in packing industry after the use can, be utilized as a sealant in coating urea fertilizer. The laboratory level product can be improved by employing sophisticated coating devices. Among the PCU systems studied MMA- DVB-TC system showed better slow release character. PCU systems can release urea in a controlled manner and will be useful in minimizing air and water pollution as well as in increasing urea efficiency.

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