Membrane-Encapsulated Controlled-Release Urea Fertilizers Based on Acrylamide Copolymers

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SYNOPSIS

About 40–70% of the applied urea fertilizer is lost to the environment, causing serious pollution. Controlled-release technology is useful in increasing the efficiency of fertilizer urea as well as in checking environment pollution. Four laboratory-level controlled-release urea fertilizers were formulated based on polymers which are soil conditioners and then evaluated for their slow-release property. Urea was coated with the copolymer of acrylamide and divinylbenzene/*N,N'*-methylenebisacrylamide/tetraethyleneglycol diacrylate or pentaerythritol triacrylate and sealant materials (wax and polystyrene). Urea coated with copolymer of acrylamide–tetraethyleneglycol diacrylate was found to be having a better slow-release property among the systems prepared. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The rate of food production needs to be further increased to keep in pace with the world population explosion for which fertilizers are to be applied in large quantities. Nitrogen is the most vital nutrient for the crops. Among the nitrogenous fertilizers, the most widely used one is urea, because of its high nitrogen content (46%) and comparatively low cost of production.[1,2] However, the efficiency or plant uptake of urea is generally below 50%. The losses are due mainly to surface runoff, leaching, and vaporization.[3–5] The lost urea causes very serious environment problems.[6] One of the methods to effectively check these losses is to encapsulate fertilizer urea granules with polymers. These materials do not allow free dissolution of urea in a soil solution; instead, water may diffuse through the polymer membrane and cause the urea to dissolve, which, subsequently, comes out through the polymer. These types of slow- or controlled-release fertilizers have many advantages over the conventional type, such as a sustained supply of minerals for a longer time, thus increasing the fertilizer use efficiency and decreasing application frequency and environmental pollution.[7,8]

Application of polymers in agriculture is a growing field of interest.[9,10] Acrylamide polymers find extensive application in tackling several problem soils to make them cultivable. Polyacrylamide, when applied to soil, interacts with clay particles and becomes linked to it through irreversible bonds. Being nontoxic to plants and animals, it is widely used as a soil conditioner. Polyacrylamide has been found effective in increasing infiltration and reducing runoff and erosion. When applied through irrigation water, polyacrylamide increases irrigation efficiency also. Thus, it creates a favorable soil condition for plant growth. Moreover, it is not affected by soil microbes, but becomes degraded in soil by mechanical breakage. Polystyrene is used here as a sealant material for coating and has also been reported to be a good soil conditioning material to improve air permeability.[11–14]

We attempted to incorporate urea fertilizer into polyacrylamide, but the desired slow-release property as well as its free-flowing nature were not observed for the product. To impart properties like rigidity and proper hydrophobic–hydrophilic balance, crosslinked polyacrylamide using divinylbenzene (DVB), *N,N'*methylenebisacrylamide (NNMBA), tetraethyleneglycol diacrylate (TTEGDA),

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and pentaerythrytol triacrylate (PETA) as crosslinking agents was prepared and used for a coating to formulate controlled-release urea fertilizers.

Our object was to prepare controlled-release urea fertilizers using polymeric soil conditioners. Here, we discuss the lab-level preparation of four controlled-release urea fertilizers based on acrylamide copolymers and an evaluation of their slow-release behavior.

EXPERIMENTAL

Laboratory-level Preparation of Polymer-coated Urea Fertilizers (PCUF)

Polyacrylamide crosslinked with DVB/NNMBA/TTEGDA or PETA were used as the coating materials for fertilizer urea. Among the crosslinking agents, DVB is rigid and hydrophobic in nature. TTEGDA is very flexible and hydrophilic and NNMBA is in between DVB and TTEGDA in these properties. PETA is a trifunctional hydrophilic monomer and was included in the study to determine the suitability of the peculiar three-dimentional net structured copolymer that it forms with acrylamide as a coating material. Wax and polystyrene were used as sealant materials for the coating. The polystyrene used here is the expanded type, widely used in the packing industry, usually known by the name "thermocol" (TC) and we used the waste TC which seldom finds any use.

The free-radical solution polymerization technique was used for the preparation of polymers used for the coating. The monomer, viz., acrylamide (2.21 g), and the crosslinking agent (DVB, 0.38 mL/NNMBA, 0.23 g/TTEGDA, 0.41 mL or PETA, 0.50 mL) were dissolved in chloroform (25 mL) containing the initiator azobisisobutyronitrile (0.1 g). Fertilizer-grade urea granules (25 g) of approximately 1 mm size were added to the solution. The temperature was raised to 40°C using a water bath while the contents were constantly stirred. The resultant net structured polymer encapsulates the urea granules. As this process continues, wax (1.00 g) and TC (1.00 g) were dissolved separately in a minimum quantity of chloroform and the solutions were added. Stirring and heating were continued and the solvent was completely evaporated and condensed out. The coated product was dried in an oven. The dried product was recoated using same amount of monomers and sealants following the same methodology.

Slow-release Behavior of PCUF

The PCUF samples were estimated for their urea content by crushing a known weight of the sample and extracting the urea in water quantitatively. The extract was estimated for the urea content.

An experiment was conducted to assess the loss of urea by leaching from the prepared coated fertilizers. PCUF samples equivalent to 200 mg N were placed on top of the soil column (1 kg, 2 mm) in a PVC tube of 90 mm diameter and were covered by a thin layer of soil. Before starting the experiment, the soil was preequilibrated by passing the 0.01*M* $CaCl_2$ solution through it for 3 days. The soil samples were leached using the 0.01*M* $CaCl_2$ solution (100 mL) on the 1st, 2nd, 7th, 14th, 21st, 28th, and 45th day after the addition of PCUF. The leachate was collected and estimated for NH_4^+—N and urea–N. Blank and control experiments, viz., with no fertilizer and with uncoated urea, respectively, were also carried out.

An incubation experiment was also carried out to study the slow-release behavior of PCUF in soil. PCUF equivalent to 20 mg N was well mixed with soil (100 g, 2 mm) and kept in a plastic beaker properly covered and incubated for different periods at 28°C. Throughout the experiment, the soil was maintained at 50% water-holding capacity by weighing and adding distilled water if necessary, periodically. Control and blank experiments were also carried out. The soils were extracted using the 0.01*M* $CaCl_2$ solution after each incubation period (2, 7, 14, 21, and 28 days) and estimated for NH_4^+—N and urea–N.[15]

All experiments were carried out in triplicate and the results were analyzed using two factorial completely randomized designs. NH_4^+—N was estimated by the Kjeldahl method of distillation and urea–N was estimated by the *para*-dimethylaminobenzaldehyde colorimetry method.[16,17]

RESULTS AND DISCUSSION

The urea contents in different PCUF samples are shown in Table I. The results of the leaching studies

Table I Urea Content (%) of PCUF Systems

PCUF Systems	Urea Content (%)
DVB	84.1
NNMBA	88.1
TTEGDA	81.6
PETA	82.7

Table II Total N (%) Leached from PCUF and Control Systems

Time (days)	Systems				
	DVB	NNMBA	TTEGDA	PETA	Control
1	22.9	24.0	20.0	23.3	42.4
2	23.1	24.4	20.8	20.3	41.6
7	22.2	23.3	20.9	25.4	5.5
14	8.4	8.7	7.0	13.3	1.3
21	4.0	3.1	5.9	4.9	0.8
28	1.5	1.5	3.9	1.6	0.4
45	0.3	0.8	2.8	0.3	0.2

CD = 0.95.

are given in Tables II and III. Table II represents the total N (%), therefore, the NH_4^+—N + urea-N, leached at different time intervals from the PCUF samples and uncoated urea-applied soil systems. More than 80% of the applied N was leached out from the uncoated urea by the 2nd day, and on 7th day, the amount of leached N had drastically decreased; on subsequent days of the study, it also continued decreasing (Table II). This is expected in the case of the conventional use of urea or any other chemical in the uncontrolled form to a system. Here, the fertilizer N content leached increases and decreases very sharply within a very short period of 7 days. The behaviour of all PCUF are significantly different from the control, and in all cases, the leached total N on the 1st and 2nd days is much lower than that of the control, and on the 7th day, the coated fertilizers, viz., DVB, NNMBA, TTEGDA, and PETA systems, leached 22.2, 23.3, 20.9, and 25.4% of total N against a significantly lower amount of 5.5% by the control (Table II). On subsequent days also, a considerably higher amount of total N leached out from the different PCUF systems than from the control. Among the PCUF, the TTEGDA system shows a better slow-release character than do all the others. In the TTEGDA system, the initial release of urea is gradual and reaches a maximum and, thereafter, it decreases very slowly, a typical behavior of slow-release systems. From the TTEGDA system, the total N leached was significantly lower up to the 14th day and, thereafter, it is significantly higher till the 45th day than in any other system (Table II). Here, an effective fertilizer N concentration in the system remains for a much longer period; hence, pollution can be checked as well as the efficiency improved. There is no considerable difference among the DVB, NNMBA, and PETA systems in the amount of N leached on all days of the experiment. However, the PETA system leached a significantly higher amount of total N on the 7th and 14th days than did the DVB and NNMBA systems. Table III represents the cumulative total N (%) leached from the different PCUF and control systems on different days of the experiment. It clearly shows the slow-release property of all the PCUF. A significantly lower amount of cumulative total N content is noted for all the PCUF on all the experimental days than for the control.

Table III Cumilative Total N (%) Leached from PCUF and Control Systems

Time (days)	Systems				
	DVB	NNMBA	TTEGDA	PETA	Control
1	22.9	24.0	20.0	23.3	42.4
2	45.9	48.3	40.8	43.6	84.2
7	68.1	71.7	61.7	68.9	89.8
14	76.4	80.3	68.7	82.2	91.1
21	80.5	83.4	74.5	87.1	91.8
28	82.0	84.9	78.4	88.6	92.1
45	82.3	85.6	81.2	88.9	92.3

CD = 2.7.

Among the four PCUF, the TTEGDA system had a lower amount of a cumulative total N value throughout the experiment than that of the others. Among the other three PCUF systems, there is no significant difference in the cumulative total N content on the 1st and 2nd days of the experiment. However, in the DVB system, a significantly lower value for cumulative total N is noticed with the NNMBA system from 7th day and with the PETA system from 14th day.

The incubation study also clearly reveals the slow-release property of the four PCUF systems. Figure 1 represents the NH_4^+—N (%) in soil with the different PCUF systems and the control. At all incubation periods, a significantly lower value of NH_4^+—N was noticed in all PCUF than that in the control, suggesting a slow-release property for them (CD = 3.2). Except on the 28th day, on all other experimental days, the soil with the TTEGDA system had a significantly lower amount of NH_4^+—N. On the 2nd, 7th, 14th, and 21st days, the NH_4^+—N content of the soil with the DVB system is significantly lower than that of the soil with the NNMBA systems. Moreover, it significantly differs from the PETA system on the 2nd, 7th, and 14th days. Therefore, the release of urea from the TTEGDA system is gradual and slower than in the DVB system, which, in turn, is slower than in the PETA and NNMBA systems. The soil with the PETA system had a significantly lower amount of NH_4^+—N content than with the NNMBA system on the 2nd, 7th, and 14th days; however, there is no significant difference on the 21st and 28th days. Figure 2 gives the values of urea–N at different incubation periods of the soil with the PCUF and control systems. By the 7th day, there was no urea remaining in the control experiment, while a significantly higher amount of urea was present in the soil

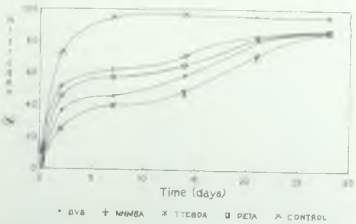

Figure 1 NH_4^+–N (%) in soil with PCUF and control systems.

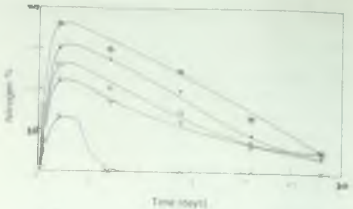

Figure 2 Urea–N (%) in soil with PCUF and control systems. ● DVB; + NNMBA; • TTEGDA; □ PETA

with all PCUF systems at all incubation periods (CD = 2.2). The fast conversion of urea to the NH_4^+ form in the uncoated urea is established again here. Moreover, the soil system will be having a very high NH_4^+—N concentration soon after the application of uncoated urea, due to which many undesired side reactions can take place or the loss of urea takes place and efficiency will be lowered. In the soil with the TTEGDA system, a significantly higher amount of urea–N is present up to the 21st day than with other PCUF systems, and even on 28th day, about 10% urea remains. Among the other three PCUF systems, the DVB system had a higher amount of urea–N up to the 21st day. The soil with the PETA system had a higher amount of urea–N than did the NNMBA system on the 2nd, 7th, and 14th days of the experiment. Thus, the slow-release behavior of the different systems are in the order TTEGDA > DVB > PETA > NNMBA.

CONCLUSION

Acrylamide copolymers, which are widely used as soil conditioners, can be used as a coating fertilizer urea to impart slow-release behavior. Urea does not inhibit or interfere with the copolymerization reaction of acrylamide and DVB/NNMBA/TTEGDA or PETA. The products formulated are controlled-release in nature. The polymerization reaction and the coating were carried out simultaneously so that an efficient and even coating could be obtained and the product was nonsticky in nature. The slow-release property is maximum for the TTEGDA system and, hence, greater than for the other PCUF systems studied. The laboratory-level product can be further improved by employing sophisticated coating devices.

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