Slow release urea—Polymeric membrane matrice for clean and efficient utilisation

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To minimise the nitrogen losses from the applied urea, the urea granules have been coated with a synthetic polymer like urea form as well as a bio-polymer like Ca-alginate. Subsequently, the nitrogen release of the resultant urea granules in water have been studied over a period of 120 h. The corresponding experimental procedure and the results obtained have been discussed.

It has been estimated that about 60% of money invested in nitrogenous fertilizers goes as waste by leaching and volatilisation leading to low nitrogen use efficiency. The ideal strategy for effective and safe-use of nitrogenous fertilizers like urea would be to incorporate the urease inhibitors into urea for minimising the ammonia volatilisation losses, to employ the nitrification inhibitors along with urea for delaying the biological oxidation of ammonical nitrogen into nitrate nitrogen and to coat the urea granules with polymeric membrane matrices for reducing their dissolution rate in water. This coating of urea granules with polymeric materials would avoid the high concentrations of nitrogen in soil at any time and diminish it’s potential to be leached into ground water, leading to a clean and efficient utilisation of nitrogenous fertilizers.

Notwithstanding, a variety of polymers have been investigated as coating materials for urea, none of them were found to be very encouraging. Coating of urea granules with ureaform (UF), which itself acts as slow-release nitrogenous fertilizer, apparently retained more nitrogen content in urea. In view of this fact, ureaform was selected as a coating material. As it was observed that ureaform obtained from Urea/HCHO whose molar ratio was less than one, after coating, yielded unsatisfactory urea granules, therefore, this ratio was kept greater than one in the present study. Moreover, algic acid derived from brown sea weeds has also been used as a model bio-polymeric matrice for nitrogen release of urea. Though Ca-alginate–beads as a matrice for the entrapment of bio-molecules/drugs have been extensively studied, it has not yet been reported on urea. It has been observed that the degradation of bio-polymeric matrices in the soil is better than synthetic polymers like ureaform.

**Experimental Procedure**

All the chemicals used were of LR grade. Urea granules containing 46.6% w/w of nitrogen were obtained from Gujarat State Fertilizers Company Limited, Baroda. A rotary type mixer with spray device was used for coating the urea granules. A Connick’s type apparatus consisting of a peristatic pump (Chemap AG, Switzerland, Model CH-8708) and glass tube with a flat end bore was used for preparing the bio-polymer based urea beads. A rotating type of laboratory microscope was used for measuring the thickness of the coated granules and the diameter of the urea beads. The values given are the average of 15 granules or beads. An automatic system (Tecator model) for nitrogen estimation was used.

Ureaform containing 7-8% moisture was prepared by refluxing urea and formaldehyde solution (37% w/v), keeping their molar ratio greater than one in a flask for 2 h. This was followed by removal of 15 mL water under reduced pressure. Urea granules to be coated were mixed with 1% binder (gum arabic) in a flask fitted to a rotary type mixer into which ureaform solution with 2-3 mL of sulphuric acid (50% w/v) was sprayed. Accordingly, UF1, UF2 and UF3 have been prepared by varying the amounts of ureaform with respect to urea (Table 1).

A homogeneous mixture of sodium alginate (0.75 g), water (10 mL) and urea granules (15 g) was

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of ureaform by wt. of urea</th>
<th>Total nitrogen content, %</th>
<th>Thickness of coating, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF1</td>
<td>05</td>
<td>42.0</td>
<td>0.25</td>
</tr>
<tr>
<td>UF2</td>
<td>10</td>
<td>43.6</td>
<td>0.35</td>
</tr>
<tr>
<td>UF3</td>
<td>15</td>
<td>44.4</td>
<td>0.45</td>
</tr>
</tbody>
</table>

*Std, error = ± 5%
Table 2—Physical data of Ca-alginate matrice urea beads

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of bio-polymer by wt. of urea</th>
<th>Total nitrogen content, %</th>
<th>Diameter of beads, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA1</td>
<td>0.5</td>
<td>33</td>
<td>2.0-2.2</td>
</tr>
<tr>
<td>CA2</td>
<td>1.0</td>
<td>39</td>
<td>2.3-2.5</td>
</tr>
<tr>
<td>CA3</td>
<td>1.5</td>
<td>40</td>
<td>2.5-2.7</td>
</tr>
</tbody>
</table>

*Std. error = ± 5%

Table 3—Comparison of urea-N losses % from UF and CA

<table>
<thead>
<tr>
<th>Time, h</th>
<th>UF1</th>
<th>UF2</th>
<th>UF3</th>
<th>CA1</th>
<th>CA2</th>
<th>CA3</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>64.5</td>
<td>54.9</td>
<td>41.9</td>
<td>25.2</td>
<td>16.0</td>
<td>10.0</td>
</tr>
<tr>
<td>48</td>
<td>8.7</td>
<td>9.4</td>
<td>7.3</td>
<td>20.0</td>
<td>14.3</td>
<td>9.1</td>
</tr>
<tr>
<td>72</td>
<td>8.5</td>
<td>9.1</td>
<td>7.2</td>
<td>13.0</td>
<td>10.0</td>
<td>8.4</td>
</tr>
<tr>
<td>96</td>
<td>8.2</td>
<td>8.8</td>
<td>7.0</td>
<td>3.2</td>
<td>7.2</td>
<td>8.1</td>
</tr>
<tr>
<td>120</td>
<td>7.8</td>
<td>8.5</td>
<td>6.9</td>
<td>0.9</td>
<td>3.0</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Total | 97.7 | 90.7 | 70.3 | 62.2 | 50.5 | 43.4 |

Prepared, transferred to a Connick’s type apparatus and was added dropwise to a gelent bath of 0.25-0.30 M calcium chloride solution under constant stirring over a period of 10 min. These falling droplets of homogeneous bio-polymer-urea solution of equal size are subsequently converted into beads by phase inversion process. Thus, formed Ca-alginate gel beads having almost same amount of urea (confirmed by batch to batch analysis of these beads) were separated and stored for gel stabilisation in a stoppered flask for 24 h. The resultant beads were spread on aluminium foil to air dry at room temperature for 3-4 days. Various formulations CA1, CA2 and CA3 were prepared by varying the amounts of sodium alginate with respect to urea (Table 2).

Two replicates of each sample of coated urea granules were tested. A known amount of granules were placed in a beaker containing 100 mL distilled water and covered with aluminium foil. After every 24 h, it was filtered and the filtrate was analysed for nitrogen. A fresh 100 mL quantity of distilled water was added to the beaker and the amount of nitrogen diffused into water from the urea granules was determined over a period of 5 days.

Results and Discussion

The percentage comparison of urea-N losses from UF and CA are shown in Table-3. The data (Fig. 1) shows that initial release of nitrogen in water was high, i.e., 64.5, 54.9 and 41.9% in the first 24 h from UF1, UF2, and UF3, respectively. However, the subsequent release of nitrogen was very gradual and after 120 h, it was 97.7, 90.7 and 70.4%, respectively.

It may be pointed out that from uncoated urea granules the release of nitrogen was over 98% within just 5 min under the similar conditions. This clearly emphasises that the ureaform coating has improved the urea-N efficiency as compared to uncoated granules. The UF3 was found to be more effective in slowing down the release of nitrogen against UF2 and UF1 which may be attributed due to its relatively high thickness of coating.

Similarly, the incorporation of urea into a bio-polymer based membrane matrice provided an excellent slow-release for nitrogen by reducing its dissolution rate (Fig. 2). The initial release rates were 25.2, 16.0 and 10% after 24 h from CA1, CA2 and CA3, respectively. The subsequent release was, however, slow over a prolonged period of time and after 120 h, the total amount of nitrogen released was 65.3, 54.5 and 43.2%. These results further emphasise that the urea incorporated with bio-polymer membrane matrice was found to be extremely
outstanding in reducing its dissolution rate as compared to UF coated urea. However, these ureas have limited applications vis-a-vis conventional urea due to the high cost of polymeric matrices involved.

**Kinetics of the N-release**—The nitrogen release pattern in UF1, UF2 and UF3 reveals that the initial release was fast in 24 h and the remaining nitrogen release was slow and very gradual. It is expected that system stabilises after initial rise and, the magnitude of this phenomenon probably is a criterion of porosity of the polymeric matrix which functions as a typical membrane, therefore, it is difficult to determine their exact order of release at a particular time. However, it is assumed to be very close to zero order rate from its total nitrogen release pattern (Fig. 1), which is supported by the fact that coated UF1, UF2 and UF3 would resemble the reservoir systems (Fig. 3) in which the fertilizer material was totally encapsulated within a rate controlling membrane. According to Fick's law, in reservoir type devices the active material is enclosed within an inert membrane, and the concentration is maintained constant within the enclosure, then a steady state will be established during which the release rate will be of zero order, i.e., constant.\(^9\,10\)

Similarly, the amount of nitrogen released from CA1, CA2 and CA3 was found to be inversely proportional to the time. Since the amount of nitrogen released at a particular time was not constant it would be difficult to determine the order of its release rate. However, it is assumed not to be of zero order, based on the fact that the bio-polymer incorporated urea would resemble the monolithic membrane systems (Fig. 4), in which the active material (urea) was dispersed or dissolved in a rate controlling matrix. This monolithic membrane systems would not have zero order release as seen in reservoir type systems.\(^8\) The active material closer to the membrane would be released first from the surface layer and the distance that active material must diffuse to reach the surface increases with time. Therefore, these systems should have slowly declining rates.\(^11\) However, in the case of CA3, it may be of a first order release rate as per its straight line seen in Fig. 4.

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**References**