

Preparation and Properties of a Double-Coated Slow-Release and Water-Retention Urea Fertilizer

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A double-coated, slow-release, and water-retention urea fertilizer (DSWU) was prepared by cross-linked poly(acrylic acid)-containing urea (PAAU) (the outer coating), polystyrene (PS) (the inner coating), and urea granule (the core). Elemental analysis results showed that the nitrogen content of the product was 33.6 wt %. The outer coating (PAAU) regulated the nitrogen release rate and protected the inner coating from damage. The slow-release property of the product was investigated in water and in soil. The possible mechanism of nitrogen release was proposed. The influences of PS coating percentage, temperature, water absorbency, and pH on the release of nitrogen were also investigated. It was found that PS coating percentage, temperature, and water absorbency had a significant influence on the release of nitrogen. However, the pH had no effect. The water-retention property of the product was also investigated. The results showed that the product not only had a good slow-release property but also excellent water-retention capacity, which could effectively improve the utilization of fertilizer and water resources. The results of the present work indicated that the DSWU would find good application in agriculture and horticulture, especially in drought-prone areas where the availability of water is insufficient.

KEYWORDS: Slow release; water retention; urea; coat

INTRODUCTION

Fertilizer and water are the important factors that limit the production of agriculture, so it is very important to improve the utilization of water resources and fertilizer nutrients. One method of improving the utilization of fertilizer involves the use of slow- or controlled-release fertilizers. Matrix type formulations constitute the first major category of slow- or controlled-release fertilizers due to their simple fabrication. The active is dispersed in the matrix and diffuses through the matrix continuum or intergranular openings, that is, through pores or channels in the carrier phase. Another way of regulating the release of fertilizer is accomplished by means of chemically controlled releasing products, such as urea-formaldehyde. The third major category of such fertilizers is coated fertilizers; that is, a fertilizer core is coated by inert materials. The release of the fertilizer is controlled by diffusion through the coating (1, 2). The materials applied most frequently as coatings are inorganic materials, such as sulfur, phosphates and silicates; synthetic organic materials, for example, dicyclopentadiene polymers (Osmocote), polyethylene (3), and ureic resins; and natural organic materials, including resin, rubber, and wax (4). However, coated slow- or controlled-granular fertilizers can be mechanically damaged during packaging, transport, and application. If the coating is damaged, the slow- or controlled-release function is lost and the granules become readily soluble.

This accelerated release could lead to short-term crop damage and long-term lack of fertilizer (5, 6).

Superabsorbent polymers can absorb large amounts of water during a short period of time. The absorbed water can be retained even under pressure. One of the most important applications of superabsorbent polymers is for agriculture and horticultural purposes, especially for effective utilization of water in dry and desert regions. Furthermore, these materials may improve soil for cultivation with regard to better soil aeration, stability, and soil erosion prevention (7). The optimized combination of superabsorbents and slow-release fertilizers may improve the nutrition of plants, mitigate the environmental impact from water-soluble fertilizers, reduce water evaporation losses, and lower the frequency of irrigation (8–10).

Using the above background and our previous studies on superabsorbent polymers and slow-release fertilizers (11–14) as a basis, we prepared in this study a double-coated, slow-release, and water-retention urea fertilizer (DSWU), whose inner coating was polystyrene (PS), and the outer coating was cross-linked poly(acrylic acid)-containing urea (PAAU). DSWU not only had a slow-release property, whose release time was more than 1 month but also could absorb water and preserve the soil moisture. These were significant advantages over the normal slow-release or controlled-release fertilizers, which generally have only a slow-release property. Furthermore, the outer coating (PAAU) could protect the inner coating (PS) from mechanical damage. The influences of the coating percentage

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of PS, temperature, water absorbency (WA), and pH on the release of nitrogen from DSWU were also studied.

MATERIALS AND METHODS

Materials. Acrylic acid (AA) was distilled at reduced pressure (boiling point = 293–294 K at 0.5 mmHg). Ammonium persulfate was recrystallized from water; N,N'-methylene bisacrylamide (NNMBA) was analytical reagent grade. PS and urea were industrial grade. All of the materials used were available from commercial sources.

Preparation and Characterization of PAAU. After 2.98 g of urea, 3.0 mL of water, and 8.0 mL of AA were added into a 100 mL beaker, the temperature was raised to 343 K using a water bath. Thereafter, 6.15 mL of ammonia was slowly added to partially neutralize the AA. A 0.0118 g amount of NNMBA as a cross-linker and 0.0806 g of ammonium persulfate as an initiator were subsequently added, and the mixture was stirred for several minutes. Then, the beaker was put in a constant temperature oven at 343 K. After 10 h, the reaction was stopped. After it was cooled, the product was ground. A white powder PAAU was obtained, which was used as the outer coating material. The nitrogen content of PAAU was 19.9%.

The ingredients of PAAU were analyzed using a Fourier transform infrared (FTIR) spectrophotometer (American Nicolet Corp., model 170-SX). The sample of PAAU was ground with dried KBr powder. The KBr disk was dried again and subjected to FTIR spectrophotometry.

Preparation of DSWU. Urea granules ranging from 2 to 2.5 mm in diameter were sieved and used for further experiments. During the sieving, we tried to remove granules that had surface defects.

The PS coating was formed by the phase inversion technique (15) using water as a precipitation bath. The 10 wt % PS coating solution was prepared by the dissolution of the solid PS in tetrahydrofuran. The temperature of the nonsolvent bath was 293 K. First, the urea granules were placed in the PS solution. Next, the granules coated with a thin layer of polymer solution were dropped into the precipitation bath where the polymer gelation took place. The precipitation bath was 0.5 m high. The falling time of the granules in the liquid was long enough to achieve the precipitation of the polymer solution. The time of the gelation was about 5 s. The coated granules were removed from the bath and dried to a constant mass at 343 K. Multiple PS coatings were prepared by immersion of the previously coated fertilizer into the PS solution followed by water precipitation. Thus, PS-coated urea (PSCU) granules with different coating thicknesses were obtained.

PSCU granules were dipped in water and then were immediately placed on PAAU powder and shaken. In this manner, PAAU could adhere to the surface of PSCU and form the outer coating. After the granules were coated, the surface of the product was cross-linked by spraying 1% (v/v) methanol solution of epoxy chloropropane and then dried in a 343 K oven to obtain the final product, i.e., the double-coated urea fertilizer.

Determination of Coating Percentage. The actual PS coating percentage was determined as follows: 10 g of PSCU was crushed and blended with water to accelerate the dissolution of urea. The solution was then filtered, and the remaining insoluble solid materials were dried in the oven until its weight became constant. The coating percentage was calculated from eq 1.

$$\% \text{ PS} = \frac{\text{weight of solid (g)}}{10} \times 100 \quad (1)$$

The actual PAAU coating percentage was determined by a gravimetric method. Ten grams of PSCU was coated with PAAU and weighed (W). The PAAU percentage was calculated from eq 2.

$$\% \text{ PAAU} = \frac{W - 10}{W} \times 100 \quad (2)$$

Determination of the Nitrogen Content. The nitrogen contents of DSWU and PAAU were determined by an elemental analysis instrument (Germany Elemental Vario EL Corp., model 1106).

Measurement of WA of DSWU. One gram of DSWU was immersed into a certain amount of water and allowed to soak at room

temperature for 90 min. The swollen DSWU was filtered through an 80-mesh sieve to remove nonabsorbed water and weighed. Per gram of dried DSWU WA was calculated using eq 3.

$$\text{WA} = \frac{M}{M_0} - 1 \quad (3)$$

where M and M_0 referred to the weight of the water swollen DSWU and that of the dry DSWU, respectively.

Slow-Release Behavior of PSCU and DSWU. All of the following tests were carried out in triplicate, and the average value was taken as the result. The influence of PS coating percentage on the nitrogen slow release of PSCU was performed as follows: 0.5 g samples were added into conical bottles containing 200 mL of distilled water. Then, the bottles were kept at 298 K in an incubator for the duration of the experiment. At certain time intervals (every 24 h), 2 mL of solution was sampled for nitrogen determination, and an additional 2 mL of water was injected into the bottles to maintain a constant amount of solvent.

The influences of WA on the nitrogen slow release of DSWU were performed as follows: 0.5 g samples were added into conical bottles containing 200 mL of distilled water, tap water, and 0.9% NaCl solution, respectively. The remaining procedures were the same as those used to measure the influence of PS coating percentage on the nitrogen slow release of PSCU.

The influences of temperature on the nitrogen slow release of DSWU were determined as follows: 0.5 g samples were added into conical bottles containing 200 mL of distilled water, and then, the bottles were put into incubators whose temperatures were set at 288, 298, and 308 K, respectively.

The influences of pH on the nitrogen slow release of DSWU were determined as follows: 0.5 g samples were added into conical bottles containing 200 mL of solution where the pH was adjusted to 4, 7, and 9. The temperature was maintained at 298 K. The nitrogen content was estimated by Kjeldahl method (C_i). The amount of nitrogen released was calculated using eq 4.

$$\text{nitrogen released (\%)} = \frac{C_i \times 0.2 \times 14}{0.5 \times 33.6\%} \times 100 \quad (4)$$

To study the slow-release behavior of DSWU in soil, the following experiment was carried out: 1 g of DSWU was well-mixed with 180 g of dry soil (below 2 mm in diameter) and kept in a 200 mL plastic beaker properly covered and incubated for different periods at room temperature. Throughout the experiment, the soil was maintained at 30 wt % water-holding capacity by weighing and adding distilled water if necessary, periodically. Blank and controlled experiments, viz., without any fertilizers and with untreated urea (the total contents of nitrogen were the same as that of 1 g of DSWU), respectively, were also carried out. The soils were extracted by 0.01 M CaCl_2 solution (9) after each incubation period (1, 2, 5, 10, 15, 20, 25, and 30 days), and the nitrogen content was estimated by the Kjeldahl method. For eight measurements, eight beakers were prepared at the same time. The amount of nitrogen released was calculated using eq 5.

$$\text{nitrogen released (\%)} = \frac{C_i \times V \times 14}{1 \times 33.6\%} \times 100 \quad (5)$$

where C_i referred to the nitrogen content obtained from the Kjeldahl method and V referred to the volume of CaCl_2 solution.

Largest Water-Holding Ratio of the Soil. The sandy soil used in this study was representative of the area of Lanzhou, which lies in the northwest of China and is a dry and semidesert region. Two grams of DSWU was well-mixed with 200 g of dry soil (below 2 mm in diameter) and placed in a 4.5 cm diameter PVC tube. The bottom of the tube was sealed by nylon fabric (with the aperture of 0.076 mm) and weighed (marked W_1). The soil samples were slowly drenched by tap water from the top of the tube until water seeped out from the bottom. After there was no seeping water at the tube bottom, the tube was weighed again (marked W_2). A control experiment, i.e., without

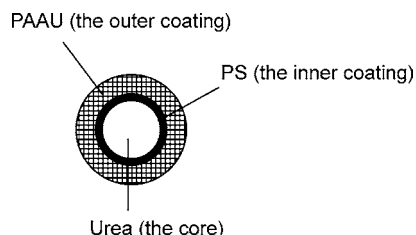


Figure 1. Cross-section schematic view of a DSWU fertilizer granule.

Table 1. Fertilizer Composition

| name of fertilizer | wt % | | | |
|--------------------|------|------|------|----------|
| | PS | PAAU | urea | nitrogen |
| PSCU1 | 4.3 | 0 | 95.7 | 44.0 |
| PSCU2 | 9.3 | 0 | 90.7 | 41.7 |
| PSCU3 | 15.1 | 0 | 84.9 | 39.0 |
| DSWU | 5.9 | 36.8 | 57.3 | 33.6 |

DSWU, was also carried out. The largest water-holding ratio ($W\%$) of the soil was calculated from eq 6.

$$W\% = \frac{(W_2 - W_1) \times 100}{W_2 - W_1 + 200} \quad (6)$$

Measurement of the Water Retention of DSWU in Soil. Two grams of DSWU was well-mixed with 200 g of dry soil (below 2 mm in diameter) and kept in a plastic beaker and then 200 g of tap water was slowly added into the beaker and weighed (marked W_1). A controlled experiment, i.e., without DSWU, was also carried out. The beakers were maintained at room temperature and were weighed every 5 days (marked W_i) over a period of 30 days. The water evaporation ratio ($W\%$) of soil was calculated from eq 7.

$$W\% = \frac{(W_1 - W_i) \times 100}{200} \quad (7)$$

Morphology of DSWU. The granules of DSWU were also subjected to a scanning electron microscopy (SEM) study. They were split into two halves, and the fractions obtained were adhered to sample holders with carbon LIT-C glue. The samples were metal coated with a layer of gold and observed in a JSM-5600LV SEM manufactured in Japan.

RESULTS AND DISCUSSION

Composition and Physical Properties of the Fertilizers.

To determine the influence of PS coating percentage on the nutrient slow-release behavior, we prepared three kinds of PSCU with different coating percentages. A number was added to the end of PSCU to identify the samples, i.e., PSCU1, PSCU2, and PSCU3. Table 1 shows the composition of all fertilizers prepared. Figure 1 shows a cross-section schematic view of a DSWU fertilizer granule. The diameters of PSCU, dry DSWU, and swollen DSWU granules in tap water were in the ranges of 2.0–3.0, 2.5–3.5, and 12–14 mm, respectively. Additionally, the crushing strength of DSWU was 1.28 kg/grain, which was about 30% greater than commercial urea pellets (whose crushing strength was 0.97 kg/grain). It was important to avoid breakage of pellets during manufacture and transport.

FTIR Analysis of PAAU (the Outer Coating Material).

Figure 2 shows the infrared spectrum of PAAU with characteristic peaks of poly(acrylic acid) (PAA) at 2947 and 2837 cm^{-1} and the characteristic absorption bands of urea at 3446, 3347, 1682, 1627, and 1464 cm^{-1} (16). The peak observed at 558 cm^{-1} corresponded to the group of $\text{N}-\text{CO}-\text{N}$, the peak observed at 1156 cm^{-1} corresponded to the group of $-\text{C}-\text{O}$,

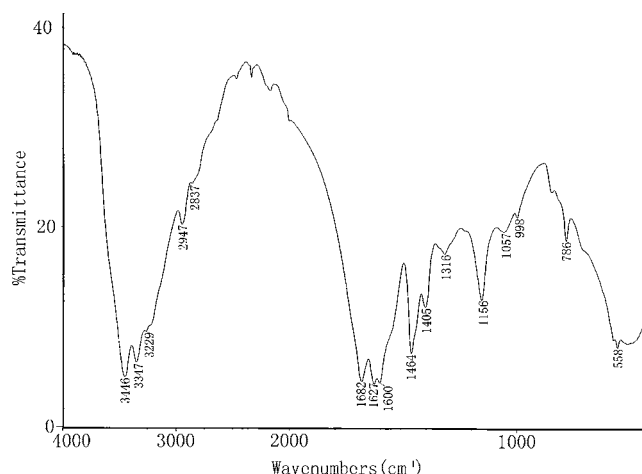


Figure 2. FTIR spectrum of PAAU.

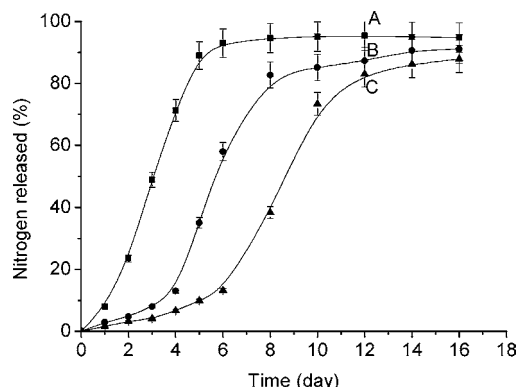


Figure 3. PSCU nitrogen release into distilled water (A) PSCU1, (B) PSCU2, and (C) PSCU3.

and the peak observed at 1405 cm^{-1} corresponded to $-\text{COO}^-$. These results proved that the PAAU consisted of PAA and urea.

Release Behavior of PSCU in Distilled Water. Figure 3 shows the nitrogen release behavior of the PSCU samples in distilled water at 298 K. The nutrient release process of polymer-coated fertilizer was described by Kobayashi et al. (17) and Shaviv (18) as follows: (i) Water (mainly vapor) first penetrates through the polymer coating; (ii) the vapor condenses on the solid urea core and dissolves part of it, thus inducing a build-up of inner pressure, under which the coating would be swollen and the diffusion apertures would be enlarged; (iii) the nutrient is released through diffusion driven by a concentration gradient across the coating, or through mass flow driven by a pressure gradient, or through a combination of the two. According to this description and the observed PSCU nutrient release behavior in distilled water at room temperature, the release processes should be divided into three stages. (i) The lag time: Water penetrates through the PS coating, but urea has not yet been released. The time of this stage is determined by the PS coating percentage and the uniformity of the coating. (ii) Constant release rate period: Urea in the core begins to dissolve and release through coating. The urea concentration in the core is very dense in this stage. The stage will last until all urea in the core dissolves completely. (iii) Declining stage: Urea in the core is dissolved completely, and the urea concentration begins to decrease.

No distinct lag time was observed for PSCU1, but there was an obvious lag time for PSCU2 and PSCU3. When the PS coating percentage is low as in PSCU1, there are always some pores or apertures on the coating; that is, the penetrability of

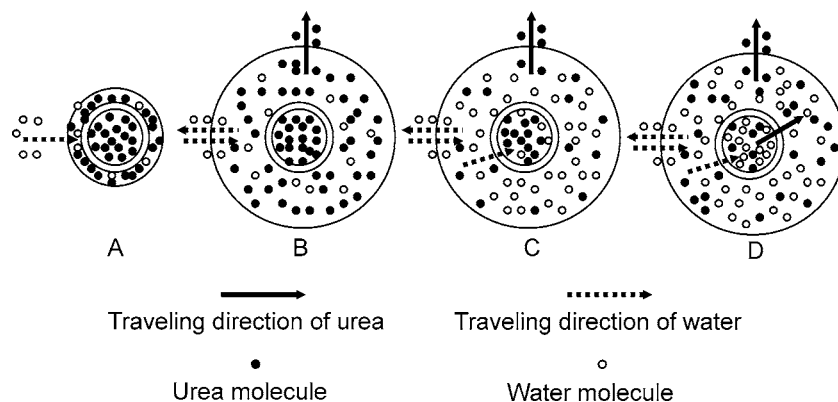


Figure 4. DSWU nutrient slow release mechanism.

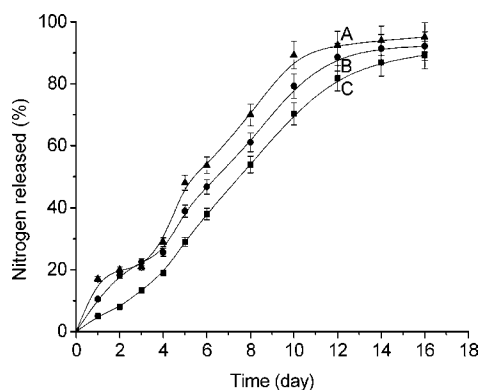


Figure 5. DSWU release behaviors at different temperatures: (A) 308, (B) 298, and (C) 288 K.

the coating is high. Thus, when PSCU1 granules are dipped into water, water can enter the fertilizer core through the imperfections on the coating and dissolve the fertilizer. Consequently, no obvious lag time was observed for PSCU1. When the PS coating percentage was 9.3%, the lag time was about 4 days (in water), while the lag time was about 7 days for PSCU3. After the lag time, about 70% nutrient was released after 3 days regardless of the samples. This could be called a “burst effect” characterizing the constant release rate period. In the third stage, viz. declining stage, the nutrient released slowly. This could be called a “tailing effect”. In a constant release rate period, the accelerated urea release could lead to short-term crop damage and long-term absence of fertilizer. If the polymer coating was damaged during packaging, transport, and application, a minimization of slow-release property of polymer-coated fertilizer would be realized. This could be eliminated by coating the PSCU with another coating material, PAAU. The existence of the outer PAAU coating not only could protect the PS coating from mechanical damage but also could help adjust the urea release rate. At the same time, the PAAU coating could absorb water during irrigation or raining days and release water during a dry time. Therefore, the double-coated urea would help maintain soil moisture.

Release Behavior of DSWU in Distilled Water. During the preparation of DSWU, we chose PSCU2 sample as the core to be coated because it had a high nitrogen content and favorable release behavior. The release behavior of DSWU in distilled water at 298 K is displayed in curve B of Figure 5. Comparing curve B of Figure 5 with curve B of Figure 3, we observe that release behavior of DSWU was less than that of PSCU2. There was no obvious burst effect, and urea began to release slowly after the DSWU was put into water. This behavior resulted from the PAAU coating being swollen by water and transformed to

hydrogel. Thereafter, the water in the swollen hydrogel network slowly dissolved the urea. Over time, a dynamic exchange between the free water in the hydrogel and the water in solution will develop (19, 20). The urea dissolved in the hydrogel network will slowly diffuse out of the granule through this dynamic water exchange. When the free water in the outer coating migrates to the inner coating, i.e., PS coating, the free water will penetrate the inner coatings slowly and the dissolved urea in the core as described with a PSCU granule. Urea in the core diffused first into the PAAU coating and then diffused out slowly through the exchange of free water between PAAU coating and solution. Otherwise, urea in the core must pass through the PAAU coating before it can enter into solution. So, the existence of outer coating regulated the release behavior of urea and minimized the burst effect. Meanwhile, the urea in the outer coating can release slowly during the lag time of urea core and meet the nutrient requirement of plants during this time. Furthermore, the PAAU coating can also protect the inner PS coating from mechanical damage. The mechanism of nutrient slow release from DSWU is illustrated by Figure 4.

Influence of Temperature on the Release Behavior of DSWU in Distilled Water. Figure 5 shows the urea release behaviors of DSWU in distilled water at temperatures of 288, 298, and 308 K. From Figure 5, we see that all of the curves are similar and that the temperature had a considerable effect on the urea release rate. The higher the temperature, the higher the urea release rate is. The dependence of the urea release on the temperature is mainly due to the increased diffusion rate as the temperature increases. When the temperature increases, the rate of PAAU absorbing water will increase, and then, the exchange of free water between PAAU and solution will accelerate. Therefore, urea in the outer PAAU coating, which released through the water exchange, will also release faster at higher temperatures. This will result in the increase of concentration gradient between PAAU coating and core, which was the driven force for urea release from the core, and consequently will result in the increase of urea release rate from the core. Moreover, because urea saturation concentration is affected strongly by the temperature, the increase of temperature will result in the increase of urea concentration in the core, which also contributed to the higher release rate at higher temperatures.

Influence of pH on the Release Behavior of DSWU in Distilled Water. Partially neutralized poly(acrylic acid), which is the main material in PAAU coating, is a pH-sensitive polymer, so the influence of pH on the slow release behavior of DSWU was also investigated. To match the pH of most soils, we chose three pH values, 4, 7, and 9, as the experimental conditions. However, experimentation showed that pH had no effect on the release behavior of DSWU. This was probably due to the

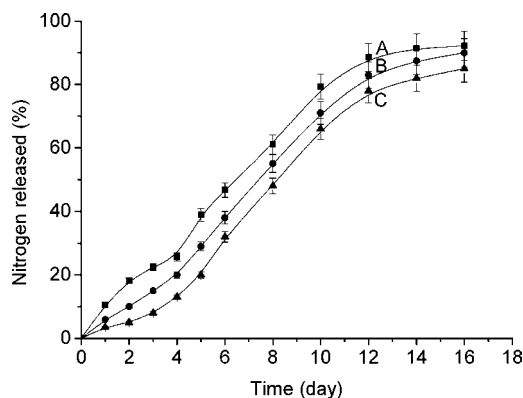


Figure 6. DSWU release behaviors with different water absorbencies (A) in distilled water, (B) in tap water, and (C) in 0.9 wt % NaCl aqueous solution.

complex of H^+ and urea (U). There were two equilibriums (21) after the partially neutralized PAAU coating was swollen.



At pH 4, H^+ complexes with the redundant urea molecules in the PAAU coating. At pH 9, UH^+ dissociates to produce H^+ . As a result, the outer PAAU coating of DSWU will not be affected by pH. The inner PS coating of DSWU was pH-insensitive. Therefore, the change of pH will not affect the slow release behavior of DSWU.

Influence of WA on the Release Behavior of DSWU in Solution. Figure 6 shows the urea release behaviors of DSWU in distilled water, tap water and 0.9 wt % NaCl solution, in which the WAs of DSWU were 142, 76, and 31 g/g, respectively. From Figure 6, we can see that all of the curves are similar, and the higher the WA, the higher the release rate was. The reason for this was because the apertures in the three-dimensional network of swollen PAA were bigger with higher WAs. As a result, the exchange of free water between the solution and the PAA network, through which urea released, was easier. Furthermore, this would result in the increase of concentration gradient between PAAU coating and core, which was the driven force of urea release from the core, and consequently results in the increase of urea release rate from the core.

Release Behavior of DSWU in Soil. Because there are obvious differences for nitrogen release between DSWU in water and in soil, we measured the nitrogen release behaviors of DSWU in soil. Figure 7 shows the release behaviors of untreated urea, a mixture of untreated urea and PAA, and DSWU in soil. As shown in curve A of Figure 7, more than 95 wt % of nitrogen was released from the untreated urea fertilizer by the first day. As shown in curve B of Figure 7, the nitrogen release rate of the mixture of untreated urea and PAA decreased as compared with the untreated urea. This result was in agreement with that of Smith and Harrison (22). However, the release rate was higher than that of DSWU. As shown in curve C of Figure 8, the nitrogen in DSWU released 10, 16, and 69 wt % by the 2nd, 5th, and 30th days, respectively. The DSWU nitrogen release did not exceed 15 wt % by the 2nd day. After 30 days, about 70% of the nitrogen was released. These results indicated that the slow-release properties of DSWU conformed to the standard of slow-release fertilizers of the Committee of European Normalization (CEN) (23).

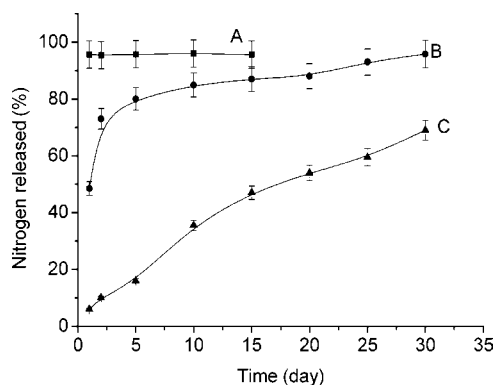


Figure 7. Nitrogen release behaviors in soil (A) untreated urea, (B) mixture of untreated urea and PAA, and (C) DSWU.

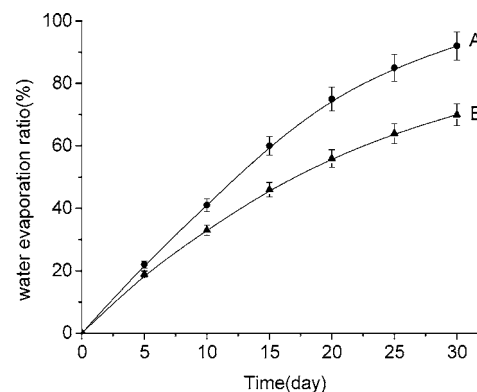


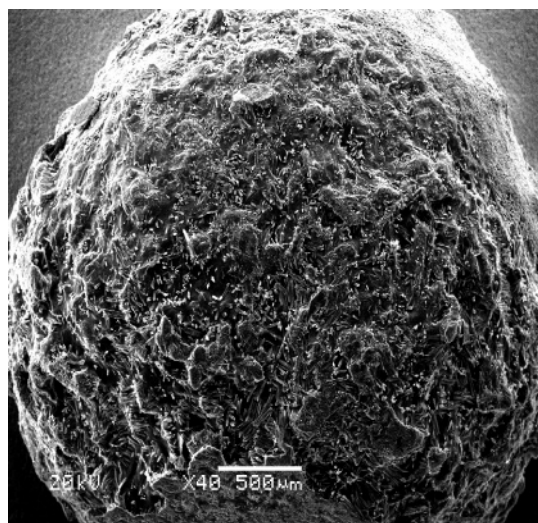
Figure 8. Water retention behaviors of DSWU (A) water + dry soil and (B) water + dry soil + DSWU.

It is well-known that urea is easily dissolved in water, so it will quickly dissolve in the soil solution after being added to the soil, and the nutrient will be quickly exhausted. While the PAA superabsorbent can absorb a lot of water in soil, the urea dissolved in soil solution can be absorbed into it and on its surface. The absorbed urea can be released or desorbed slowly through the exchange of free water or minerals between soil solution and PAA. Therefore, the mixture of PAA and urea had a slower release rate than untreated urea.

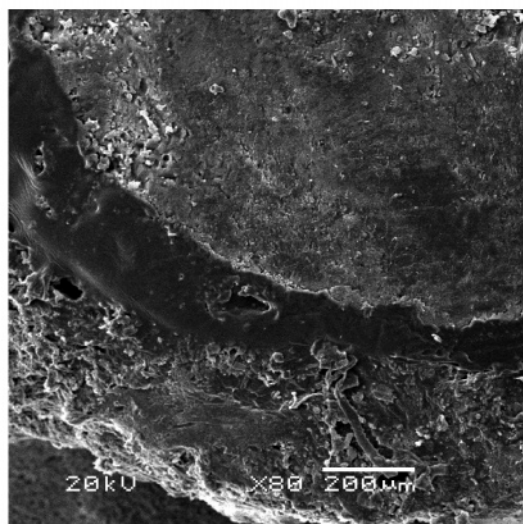
The slow-release property of DSWU in soil was similar to that in water except that the release rate was less. This was probably because there are many ions in soil, which can strongly affect the WA of PAA. The decrease in DSWU WA will cause a decrease of the nitrogen release rate. Furthermore, the free water in soil was less than that in solution; thus, this will lead to the decrease of free water exchange rate between swollen PAAU coating and soil. Consequently, the nitrogen release rate of DSWU in soil is less than that of DSWU in water.

Besides its slow-release property, the other important DSWU property is its water-retention characteristic in soil. DSWU can absorb water during raining and irrigation and thereafter release water slowly to the soil in dry times. This is especially important in drought-prone areas where the availability of water is insufficient. Therefore, experiments to test the water-holding capacity and water-retention behavior of DSWU in soil were performed.

Largest Water-Holding Ratio of the Soil. Experimentation showed that the largest water-holding ratio of the soil with DSWU was 41.8 wt %, while that of the soil without DSWU was 30.2 wt %. This indicated that the DSWU can improve the water-holding capacity of the soil. Therefore, DSWU can effectively store rainwater or irrigation water and improve the



A



B

Figure 9. SEM of the surface (A) and part of cross-section (B) of DSWU.

utilization of water resources. This is a significant advantage of DSWU over normal slow-release fertilizers.

Water Retention Behavior of DSWU in Soil. Figure 8 shows that the water retention behavior of the soil with DSWU is greater than the soil without DSWU. The water transpiration ratio of soil without DSWU reached 60.0 and 92.5 wt % on the 15th and 30th days, respectively, while that of the soil with DSWU was 46.0 and 69.5 wt %, respectively. The time needed for 50.0 wt % water evaporation was 12.5 days for the soil without DSWU, while it was 17.3 days for the soil with DSWU. After 30 days, the water content of the soil without DSWU was 7.5 wt %, while that of the soil with DSWU was 30.5 wt %. Thus, DSWU had good water-retention capacity in soil, and that with DSWU use water can be saved and managed so that they can be effectively used for the growth of plants.

This property results from the superabsorbent polymer (PAA) in the outer coating of DSWU absorbing and storing a large quantity of water and allowing the water absorbed to be released slowly when the soil moisture decreased. The swollen DSWU was just like an additional nutrient reservoir for the plant–soil system. Consequently, it prolonged irrigation cycles, reduced irrigation frequencies, and strengthened the ability of plants to fight against drought. It was also noted that lots of granular

structures could form in the soil with DSWU use. It has been reported in the literature (24) that these granular structures contributed to stabilization of the soil structure and improved aeration, permeability, and till ability of the soil, reduced soil packing and cracking, minimization of soil crusting, and thus prevention of the soil from hardening, providing a favorable environment for crops.

The study showed that besides its slow-release property, the DSWU had good water-retention and moisture-preservation capacity, which are the properties that the normal slow-release fertilizers do not have. It is especially significant for the arid and desert areas.

Morphology of DSWU. The SEM of the surface and cross-section of the DSWU are shown in Figure 9. From Figure 9A, it can be seen that the surface of DSWU is coarse and porous, which structurally increased the surface area of the DSWU. Therefore, when DSWU is dipped in water, it can absorb water quickly to form a swollen hydrogel, which is responsible for the water-retention property of DSWU. Figure 9B showed the three-layer structure of DSWU. The rough outer layer was PAAU, which could not only absorb a large amount of water and regulate the slow-release behaviors but also protect the PS coating from mechanical damage. The compact middle layer was PS, which served as a physical barrier for mass transfer and, hence, reduced the rate of water diffusion into the core and the nitrogen diffusion outside the core. The inner core was a urea granule. Thus, after the urea core is dissolved by water, it must pass through two layers, i.e., PS coating and PAAU coating, to release into the soil. This provides the DSWU with a good slow-release property. In summary, the outer PAAU layer enables the water-retention property, and the middle PS layer enables the DSWU slow-release property.

ABBREVIATIONS USED

DSWU, double-coated slow-release and water-retention urea fertilizer; PAAU, poly(acrylic acid)-containing urea; PS, polystyrene; PSCU, polystyrene-coated urea; AA, acrylic acid; NNMBA, N,N'-methylene bisacrylamide; FTIR, Fourier transform infrared; WA, water absorbency; SEM, scanning electron microscopy.

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