JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Environmentally Friendly Slow-Release Nitrogen Fertilizer

Boli Ni, Mingzhu Liu,* Shaoyu Lü, Lihua Xie, and Yanfang Wang

State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

ABSTRACT: To sustain the further world population, more fertilizers are required, which may become an environmental hazard, unless adequate technical and socioeconomic impacts are addressed. In the current study, slow-release formulations of nitrogen fertilizer were developed on the basis of natural attapulgite (APT) clay, ethylcellulose (EC) film, and sodium carboxymethylcellulose/hydroxyethylcellulose (CMC/HEC) hydrogel. The structural and chemical characteristics of the product were examined. The release profiles of urea, ammonium sulfate, and ammonium chloride as nitrogen fertilizer substrates were determined in soil. To further compare the release profiles of nitrogen from different fertilizer substrates, a mathematical model for nutrient release from the coated fertilizer was applied to calculate the diffusion coefficient *D*. The influence of the product on water-holding and water-retention capacities of soil was determined. The experimental data indicated that the product can effectively reduce nutrient loss, improve use efficiency of water, and prolong irrigation cycles in drought-prone environments.

KEYWORDS: Slow-release fertilizer, coating materials, water-holding, degradation

INTRODUCTION

Modern agriculture now feeds 6 billion people. Global cereal production has doubled in the past 40 years mainly from the increased yields resulting from greater inputs of fertilizer, water, and pesticides, new crop strains, and other technologies.[1] Globally, application of fertilizer nitrogen (N) has increased rapidly in the last several decades, from 32 million tons in 1970 to around 100 million tons in 2010; it is expected to increase to 130−150 million tons/year by 2050.[2] China is a typical developing country with a large population. Thus far, about 60% of the total population lives in the countryside, and use of fertilizers is one of the main means of increasing crop yields. From 1977 to 2005, annual synthetic N fertilizer application increased from 7.07 to 26.21 million tons (a 271% increase) in China. Large amounts of external N inputs with decreasing N use efficiency have contributed to severe environmental pollution, including the degradation of downstream water quality, eutrophication of coastal marine ecosystems, development of photochemical smog, and rising global concentration of the powerful greenhouse gas nitrous oxide.[3,4]

With the increasing public concern toward human health, environmental protection, and natural resource sustainability, there is a shift toward the development of environmentally friendly N fertilizers that sustain food production with minimal nutrient loss in runoff or leaching. In the last several decades, controlled release (CR) technology has emerged and developed as an approach toward solving the problems associated with the application of conventional agrochemicals.[5−8] The aims of CR formulation are to allow for the release of the active ingredient to the target at a controlled rate and support adequate nutrients for crop production with the optimum limits. Controlled release fertilizers (CRFs) can be classified into two basic groups: compounds of low solubility and coated or encapsulated water-soluble fertilizers. Polymer-coated CRFs look promising for widespread use in agriculture because the science and technology of polymers has undergone explosive growth during recent years and they can be designed to release nutrients in a more controlled manner.

Society is developing to a larger extent the expectation that the polymeric materials used will be renewable-based, biodegradable, recyclable, or some combination thereof.[9] Natural polymers and their derivatives used as coating materials have received considerable interest based on the characteristic properties of the polymeric molecules. Cellulose is the most abundant natural polymer and a very promising raw material at low cost for the preparation of various functional polymers. Cellulose ethers are produced by replacing the hydrogen atoms of hydroxyl groups in the anhydroglucose units of cellulose with alkyl or substituent groups.[10] In this study, ethylcellulose (EC) film with a plasticizing agent was used as a hydrophobic coating to allow for the slow release of the fertilizer nutrients; sodium carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) were used for cellulose-based hydrogel preparation.

Hydrogels are cross-linked hydrophilic polymers and can swell by absorbing a huge volume of water or aqueous solutions. This property has led to many practical applications for these materials, particularly in arid regions for improving water retention in sandy soil and the water supply to plants.[11−13] A considerable drawback for traditional hydrogels, which are usually cross-linked sodium polyacrylates, is their environmental impact. Many efforts have been made by researchers toward obtaining novel hydrogels with preferable properties based on synthetic, natural, or hybrid polymers for specific applications.[14−16] In this study, the CMC/HEC hydrogel used as fertilizer coatings was synthesized by a simple route and was expected to control nutrient release and improve the water-holding capacity of soil.

In the present study, an environmentally friendly nitrogen fertilizer was produced on the basis of attapulgite (APT) clay as a matrix and ethylcellulose film with a plasticizer and cellulose-based hydrogel as coatings. The introduction of these natural

Received: May 28, 2011
Accepted: August 17, 2011
Revised: August 16, 2011
Published: August 17, 2011

Table 1. Properties of the Soil Used in the Study

	composition				
soil texture	clay (<0.002 mm) (%)	silt (0.002−0.05 mm) (%)	sand (0.05−2 mm) (%)	pH	electroconductivity (μS/cm)
silt loam	9.27	61.89	28.84	8.13	2150

materials and their derivatives can induce biodegradability and full protection of the ecosystem. In addition, the coated fertilizer is expected to retard nitrogen release, improve soil moisture, reduce the use of water, and alleviate environmental hazards caused by excessive fertilization. Therefore, the main purpose of this study was (1) to examine the physical and chemical characteristics of the fertilizer and (2) to determine the release characteristics of the coated fertilizer and its effect on improving the water-holding capacity of soil.

MATERIALS AND METHODS

Materials. CMC [viscosity of 1300 mPa s in 1% (w/v) aqueous solution at 25 °C, with a carboxymethylation degree of 0.91 per disaccharide unit] was supplied by Wealthy Chemical Industry Co., Ltd. (Suzhou, China). HEC [viscosity of 5000−6400 mPa s in 2% (w/v) aqueous solution] was provided by Aladdin Reagent Co., Ltd. (Shanghai, China). EC [viscosity of 20−40 mPa s in 2% (w/v) ethanol solution] was provided by Shanghai Chemical Factory (Shanghai, China). Guar gum (GG, number molecular weight of 5 000 000) was obtained from Beijing Guaerrun Technology Co., Ltd. (Beijing, China). Citric acid and stearic acid were provided by Tianjin Chemical Factory (Tianjin, China). Cellulase, obtained in powder form from Aladdin Reagent Co., Ltd. (Shanghai, China) with an activity of 10 units mg^{-1}, was stored in a refrigerator. Natural APT (supplied by Gansu Haozhou APT Co., Baiyin, China) was milled and sieved through a 200-mesh screen before use. The soil used in the study is a representative sample in Lanzhou, which lies in northwest China. The properties of the soil are shown in Table 1.

Synthesis of the CMC/HEC Hydrogel. A series of samples with different amounts of CMC, HEC, and cross-linker citric acid were prepared according to the following procedure. In a typical reaction, 15 g of CMC and 7.5 g of HEC were dissolved in 750 and 150 mL of water, respectively. After that, the solution of CMC and HEC was mixed well by stirring gently until a clear solution was obtained. Then, 0.7 g of citric acid was added. Finally, the reaction solution was poured into a container (solution height of 1 cm) and dried at 90 °C. The resultant product was milled, screened, and stored for further use.

Preparation of Coated Slow-Release Nitrogen Fertilizer. Using urea as an example, the preparation of coated slow-release nitrogen fertilizer is as follows. An amount of urea and APT was ground to powder and mixed well. Then, the mixture was fed into a rotating pan with urea granules (about 1.0−1.3 mm in diameter) in batches. During this step, the granules as fertilizer cores with a desired range of sizes were obtained under water atomization. Subsequently, EC and stearic acid were mixed at the ratio of 5:2 (w/w) in ethanol. Then, the solution (3.5%, w/v) was sprayed on the fertilizer cores to form the inner coating. Finally, CMC/HEC hydrogel powder (below 110 mesh) as the outer coating was coated onto the surface of the granules under rotation. The granulated product was fed into a dryer to remove excess water and to harden the granules. The dried product was passed over a screen where the particles smaller or larger than the desired size were removed. The preparation of the coated fertilizers with $(NH_4)_2SO_4$ or NH_4Cl as substrates was the same as above.

Coated Granule Characterization. Fourier transform infrared (FTIR) spectroscopy of CMC, HEC, and CMC/HEC hydrogel was carried out with a KBr disk using a Nicolet NEXUS 670 FTIR spectrometer.

The content of nitrogen in the coated fertilizers was determined by an elemental analysis instrument (Germany Elemental Vario EL Corp., model 1106).

The average diameter of coated fertilizers was determined using a micrometer for 20 granules.

The surface morphology of the coated and uncoated fertilizer granules was examined with scanning electron microscopy (SEM) (Hitachi, model S-4800, Japan).

Fertilizer granules should have sufficient mechanical strength to withstand normal handling and storage without fracturing. The crushing strength of granules, which is the minimum force required for crushing the granules, is measured by applying pressure to individual granules. The crushing strength test is a valuable tool in helping the manufacturer tune the granulation process to produce products with maximum attainable hardness. In this study, the average crushing strength was measured using compressing equipment for 30 granules (2.7 ± 0.3 mm in diameter).

The percentage of water by weight in a fertilizer is known as the moisture content of the fertilizer. Knowledge of the moisture content is crucial because it can be used as a product quality indicator and management tool for its storage, shipment, and handling. Typically, the moisture content of fertilizer is determined by drying and weighing techniques. In this study, the moisture content of the coated fertilizer was determined by drying 10 g of the coated fertilizers in a vacuum drying chamber at 50 ± 2 °C until there was no change in the mass of the sample.

Measurement of Water Absorbency of the CMC/HEC Hydrogel. The accurately weighed CMC/HEC hydrogel (0.2 g, 40−90 mesh) was immersed into a certain amount of tap water and allowed to soak at ambient temperature for 60 min. The swollen polymers were filtered and weighed. The water absorbency (WA) was calculated using eq 1

$$\mathrm{WA} = (M - M_0)/M_0 \qquad (1)$$

where M and M_0 refer to the weight of the swollen and dried superabsorbents, respectively.

Slow Release Behavior of the Coated Fertilizers in Soil. Soil samples (0−10 cm in depth) used in this study were dried at room temperature for 2 weeks and then passed through a 26-mesh sieve. A total of 10 g of this soil and 50 mL of deionized water were added to a bottle and stirred for 1 h. Then, the soil pH and electroconductivity were determined on the suspension with a pH meter (PHS-3B, Shanghai Leici, China) and a conductivity meter (DDS-307, Shanghai Leici, China), respectively.

The release rate of nitrogen (N) from urea, ammonium sulfate, and ammonium chloride was determined by burying 1 g of coated fertilizer in sealed plastic mesh bags approximately 6 cm below the surface of the soil at ambient temperature. Throughout the experiment, the soil moisture was kept at 20%. After 0.5, 1, 2, 3, 5, 10, 15, and 20 days, the mesh bags were retrieved and placed in a paper bag and air-dried. Then, the fertilizer granules were removed from the mesh bags and assessed for nitrogen content.

Measurement of Water-Holding and Water-Retention Capacity of Soil with the Coated Fertilizers. The study of the effect of the coated fertilizers on water-holding and water-retention capacity of soil was carried out. Different amounts of the coated fertilizers were mixed with 200 g of dry soil (below 26 mesh) and placed in a 4.5 cm diameter polyvinyl chloride (PVC) tube. The bottom of the tube was sealed with nylon fabric and weighed (marked W_1). The soil sample was

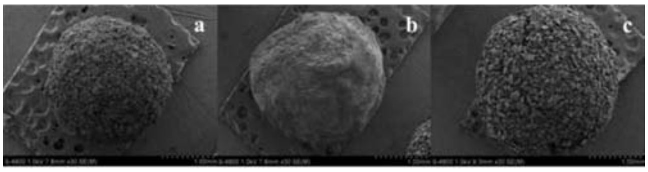


Figure 1. Morphologies of the (a) fertilizer core, (b) fertilizer core with the inner coating, and (c) final product with the inner coating and outer coating.

Table 2. Characteristics of the Coated Fertilizers

	fertilizer type		
characteristics	urea	$(NH_4)_2SO_4$	NH_4Cl
diameter of the dry sample (mm)	2.4−3.0		
inner coating content (%)	3.5−5.5		
outer coating content (%)	7−10		
nitrogen content (%)	24.9	15.0	16.5
moisture content (%)	2.1	2.2	2.5
average crushing strength (N)	18.1	6.5	3.5

slowly drenched by tap water from the top of the tube until water seeped out from the bottom. When no water seeped at the bottom, the tube was weighed again (marked W_2). A control experiment without the coated fertilizers was also carried out. Three fertilizer application rates (1, 2, and 3%) were examined. The water-holding capacity (WH %) of the soil was calculated from eq 2.

$$\text{WH \%} = (W_2 - W_1) \times 100/200 \qquad (2)$$

Enzymatic Degradation of the CMC/HEC Coating. Enzymatic degradation studies were carried out in an acetic acid/sodium acetate buffer at pH 5.0 with cellulase. In a typical experiment, preweighed dried polymer samples (15 × 10 × 0.1 mm) were added to 50 mL of the enzyme solution for a given time. The enzyme concentration was 0.1 mg/mL. Tests were carried out at 25 °C, without shaking. After incubation, the samples were immersed in an excess of distilled water to wash away the degraded polymer. Finally, the hydrogels were dried under vacuum. The extent of degradation was calculated from eq 3

$$\text{degradation (\%)} = (m_0 - m_d) \times 100/m_0 \qquad (3)$$

where m_0 and m_d are the initial and final weights (before and after degradation) of the dry samples.

RESULTS AND DISCUSSION

Morphology and Characteristics of the Coated Fertilizers. Figure 1 shows the morphology of the fertilizer core (Figure 1a), the fertilizer core with the inner coating (Figure 1b), and the final product with the inner coating and outer coating (Figure 1c). As can be seen from Figure 1b, the surface of the fertilizer was smooth because of the EC film, which could prevent the moisture from permeating through it into the fertilizer cores. Figure 1c shows that fine particles of the CMC/HEC hydrogel covered the surface of the fertilizer. Holes existed between these fine particles; therefore, water can be absorbed easily by the product because it had a high specific surface area. The characteristics of the coated fertilizers are presented in Table 2.

FTIR Analysis of CMC, HEC, and CMC/HEC. The FTIR spectra of CMC, HEC, and CMC/HEC are shown in Figure 2.

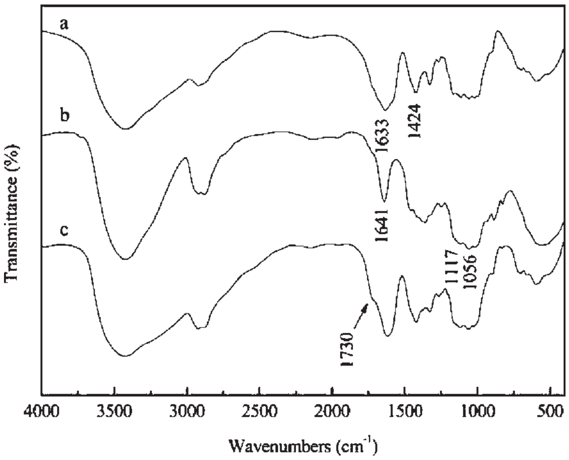


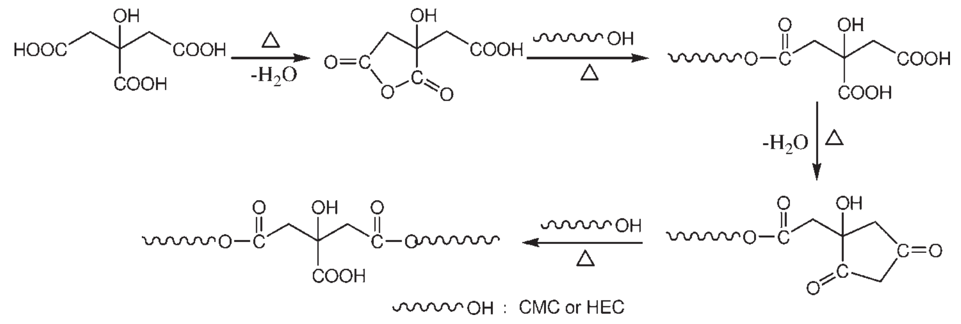
Figure 2. FTIR spectra of (a) CMC, (b) HEC, and (c) CMC/HEC hydrogel.

In the spectrum of CMC (Figure 2a), the peaks observed at 1633 and 1424 cm^{-1} can be attributed to the $-COO^-$ asymmetric and symmetric stretching vibration, respectively. Some characteristic peaks in the HEC spectrum (Figure 2b) can be ascribed to 1641 cm^{-1} for the absorption of water in HEC, 1117 cm^{-1} for the C−O−C stretching vibration, and 1056 cm^{-1} for the C−O-(H) stretching vibration, respectively. In the spectrum of CMC/HEC (Figure 2c), the new peak observed at 1730 cm^{-1} can be attributed to the C=O stretching of ester, indicating the cross-linking reaction of CMC and HEC with citric acid. Scheme 1 shows the possible mechanism of the cross-linking reaction. When citric acid is heated, it will dehydrate to yield the cyclic anhydride that will react with cellulose ethers; successively another cyclic anhydride can be achieved into the citric acid structure through the other two nonreacted carboxylic groups. Further reaction with cellulose ethers can then lead to cross-linking.

Water Absorbency Determination. One of the important properties of the coated fertilizers is the water absorbency because of the coating of CMC/HEC hydrogel materials. To improve the water absorbency capacity of the product, the reaction parameters were optimized. The effect of the CMC and HEC contents on water absorbency of the hydrogel is shown in Figure 3 (reaction conditions include the total polymer concentration of the reaction solution, 2 wt %; CA content, 3.5 wt %; and reaction temperature, 90 °C). The water absorbency increases when the ratio of CMC/HEC is larger than 3:1 and decreases with the lower ratio. The reason for the change can be explained as follows. HEC is less sterically hindered than CMC and can react more quickly than CMC. In addition, in each repeating unit, HEC has more hydroxyl groups than CMC (see Scheme 2). When the CMC content is high, the cross-linking density of the network is low, which in turn results in an increase in soluble materials.[17] Meanwhile, with the increasing of the CMC content, the screen effect of the sodium ions on the polyanion chains will reduce the electrostatic repulsion of the network, which results in the decrease of water absorbency of the CMC/HEC polymers. When the ratio of CMC/HEC is lower than 3:1, a further increase in the HEC content results in the cross-linking degree increasing, which consequently causes a decrease in the water absorbency.

Recently, polycarboxylic acid has been used as promising cross-linking agents for cellulose and cellulose derivatives among the various new regents investigated.[18−20] Citric acid, an intermediate

Scheme 1. Possible Mechanism of the Cross-Linking Reaction of CMC and HEC



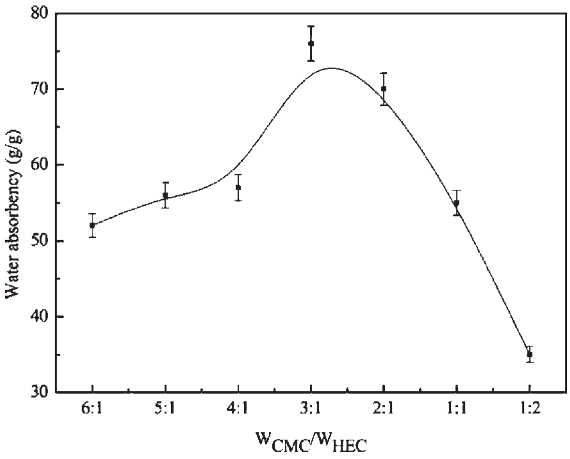


Figure 3. Effect of the CMC and HEC contents on water absorbency of the CMC/HEC hydrogel.

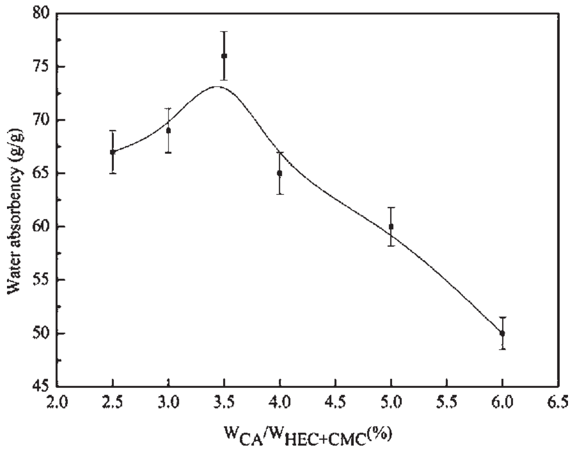
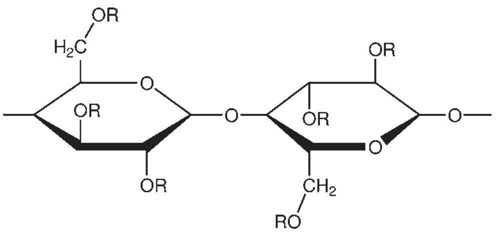


Figure 4. Effect of the citric acid content on water absorbency of the CMC/HEC hydrogel.

Scheme 2. Structure of CMC and HEC



CMC: R=H or CH_2COONa
HEC: R=H or CH_2CH_2OH

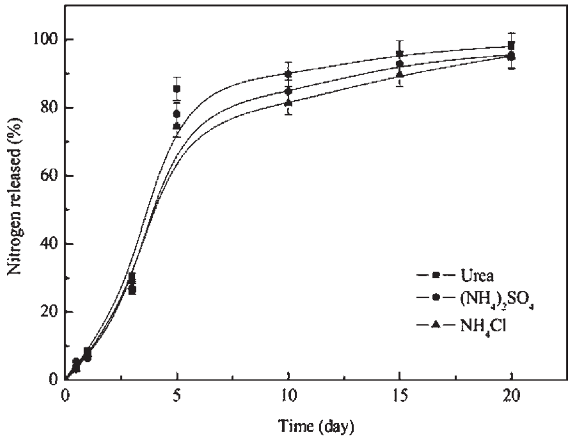


Figure 5. Slow-release behavior of nitrogen (N) from three kinds of coated fertilizers: (a) urea, (b) ammonium sulfate, and (c) ammonium chloride.

of the tricarboxylic acid cycle, is one of the most important commercially valuable products because of its widespread use in food, pharmaceuticals, and others.[21,22] In this work, citric acid was used as a cross-linker in the synthesis of CMC/HEC hydrogel materials. The water absorbency as a function of the citric acid content was investigated for cross-linked CMC/HEC hydrogel, as shown in Figure 4. As we can see from the figure (reaction conditions include the total polymer concentration of the reaction solution, 2 wt %; ratio of CMC/HEC, 3:1; and reaction temperature, 90 °C), the water absorbency increases when the cross-linker content is lower than 3.5 wt %. This is due to incomplete conversion of the cross-linking process, leading to an increase in soluble materials. When the citric acid content is larger than 3.5 wt %, the number of cross-linking points increases in the hydrogel networks, which results in a reduction in the mesh size of the voids available between the network chains. This obviously restricts relaxation of network chains, thus resulting in a fall in the water sorption capacity of the hydrogels.

Slow-Release Behavior of the Coated Fertilizers in Soil. The release rates of different coated fertilizer substrates were monitored until no more significant amount of each substrate was released. Three kinds of nitrogen fertilizers (urea, ammonium sulfate, and ammonium chloride) were used for the release experiment, and the release kinetics in soil at room temperature are depicted in Figure 5. As shown in the figure, the release profiles of the three fertilizer substrates consist of three stages. During the first stage, within 24 h, soaking and penetration of water vapor into the fertilizer granules dissolved a small fraction of solid fertilizer. This stage is characterized by a slow-release rate of nutrient elements. This is mainly due to the diffusion barrier of hydrophobic EC coating. The nitrogen in the coated fertilizers released 8.7, 6.3, and 7.6% for urea, ammonium sulfate, and ammonium chloride, respectively. A possible explanation for this stage is the time needed to fill the internal voids of the granule with a critical water volume.[23] The second stage from 1 to 5 days was characterized by a steady release of significant quantities of nitrogen. The dissolved fertilizer substrates diffused out from the EC coating, entered the CMC/HEC layer, and then released in soil through the dynamic exchange of free water. During the third stage, from 10 days to the end of the experiment, the concentration of the internal solution decreased because of the continuing concomitant fluxes of nutrient released out and water flowed into the granule. Meanwhile, APT was used as a matrix in this study, which has a high special surface area, and there are many parallel channels through the lattice.[24] When water diffused into fertilizer cores, part of the nutrients would be adsorbed by APT, which consequently slowed the release rate of nutrients. APT has a crystal lattice with a net negative charge, causing the mineral to absorb cation molecules (NH_4^+ in this study) to balance the charge deficit, which consequently slowed the release rate of nutrients. From Figure 5, we can also see that the release rate of urea is higher than that of ammonium sulfate and ammonium chloride, which conforms reasonably well with the solubility of urea, ammonium sulfate, and ammonium chloride (water solubility at 20 °C is 105, 75, and 37 g/100 mL, respectively). Fertilizer solubility may affect the solute concentration gradient between the fertilizer granules and the external environment, thus affecting the flux of nutrient release.

To further compare the release profiles of nitrogen from different fertilizer substrates, the release data of the coated fertilizers in soil were analyzed by applying the mathematical model proposed by Al-Zahrani[25]

$$\frac{M_t}{M_0} = 6(1 + \alpha)\left(\frac{tD}{\pi R^2}\right)^{0.5}$$

$$\alpha = \frac{C_\infty}{C_0 - C_\infty}$$

where M_t/M_0 is the ratio of active ingredient released at time t, D is the diffusion coefficient, R is the radius of the fertilizer granule, C_0 is the initial concentration of the fertilizer, and C_∞ is the concentration of the fertilizer in the sphere at infinite time. The equation works well for analyzing the release rate of fertilizers from spherical membranes. The data of the slow-release experiment show that more than 95% of the nitrogen was released from the three different fertilizers during 20 days. Therefore, C_∞ should be 0 in this study. The diffusion coefficient (D) of nitrogen was calculated to be 0.035, 0.031, and 0.029 mm^2/day for urea, ammonium sulfate, and ammonium chloride, respectively. The values of D can be used as a better tool to design fertilizers and choose coating materials to obtain required release characteristics.

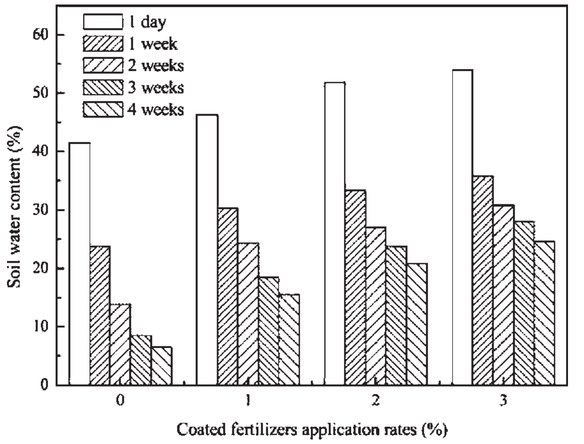


Figure 6. Water-holding and water-retention capacities of soil with different application rates of the coated fertilizers.

It is important to note that the nitrogen release behaviors and the granule efficacy are predicted to be different when the coated fertilizers are applied to different soils under different environmental conditions. More extensive experiments on this topic should be carried out in further studies for the practical application.

Effect of the Coated Fertilizers on Water-Holding and Water-Retention Capacity of Soil. The presence of water in soil is essential for vegetation growth. Liquid water ensures the feeding of plants with nutritional elements, which increases the growth quality of plants.[13] Sandy soils are characterized by low water-holding capacity and excessive drainage of rain and irrigation water below the root zone, leading to poor water and fertilizer use efficiency by crops. Taking into account the interestingly particular characteristic of the water absorption capacity of the coated fertilizers prepared in this study, we studied its effect on water-holding and water-retention capacity of soil. As shown in Figure 6, the water-holding capacity of soil (1 day) is 46.3, 51.8, and 54.0% for the coated fertilizer application rate of 1, 2, and 3%, respectively, and that of soil without coated fertilizer is 41.5%. It is noted that soil/coated fertilizer mixtures retain more water than the control soil and the water content increases with an increasing amount of the coated fertilizers in the soil. However, in comparison to the water retained by the free hydrogels in tap water, the soil/coated fertilizer mixtures retain much less water. First, in the mixtures, each granule is surrounded by soil particles and subjected to a confining pressure by these particles.[11] Second, the presence of ions in soil solution makes the osmotic pressure difference between the polymeric network and the external solution decrease, resulting in a decrease in the water absorbency of the CMC/HEC hydrogel. Meanwhile, the penetration of cations (such as Na^+, K^+, Ca^{2+}, and Mg^{2+}) into the polymer network makes the screening effect of them on the anionic group ($-COO^-$) in the polymeric network more evident.[26,27] Therefore, the swelling degree of the CMC/HEC hydrogel in soil is limited in comparison to that in tap water. However, in comparison to the control (soil without the coated fertilizers), the product effectively improved the water-holding capacity of soil, even at low application rates. From Figure 6, we also find that the soil moisture after 2 weeks is 13.8, 24.3, 27.0, and 30.8% for the coated fertilizer application rate of 0, 1, 2, and 3%, respectively. The untreated soil loses almost all of the water after 4 weeks, whereas 15.5% of the initial absorbed water of the soil mixed with 1% coated fertilizer can still remain. The reason is that the outer coating of the coated fertilizers could

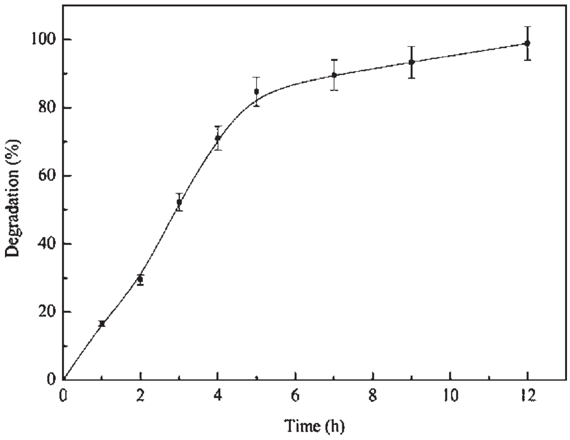


Figure 7. Degradation of CMC/HEC coating materials in cellulase solution.

absorb a large quantity of water and let the water release out slowly with the decrease of soil moisture. The coated fertilizers will be used for improving use efficiency of water and prolonging irrigation cycles in drought-prone environments, as modeled in our study. However, the results are predicted to be different from a real soil environment with its complexity together with weather conditions during plant growth and development, which will affect the water-holding and water-retention capacity.

Degradation of CMC/HEC Coating Materials. In the production of coated or encapsulated fertilizers, the materials applied most frequently as coatings are sulfur, waxes, polyethylene, polystyrene, and polyesters. Application of sulfur-coated urea may increase the acidity of the soil, because both sulfur and urea contribute to increased acidity. Moreover, some types of polymers used in the coating of conventional fertilizers currently in use decompose extremely slowly or not at all in the soil. Their use may thus lead to an undesirable accumulation of plastic residues.[5] Therefore, environmentally safe, degradable coating materials are expected to be used. In this study, cellulose-based hydrogel was synthesized and used as fertilizer-coating materials. Figure 7 shows the weight loss of the CMC/HEC hydrogel as a function of the degradation time. As shown in the figure, the degradation of the hydrogels proceeded at a higher rate during the first 5 h and then slowed. After 5 h, the percentage of degradation was 71%, and the hydrogels degraded completely within 12 h. However, in soil, the degradation rates for CMC/HEC hydrogels were predicted to be much slower because cellulase levels were much lower than those used in the study. The mechanism of degradation can be described as the following. Hydrogel materials interact with surrounding fluids by absorbing water, which initiates the degradation process. Moreover, the high water absorbency of the CMC/HEC hydrogel accelerates the degradation process. In the surface erosion, the cellulase molecules invade the surface of the polymeric materials and cleave $\beta(1-4)$-linked glucose units of CMC and HEC.[28,29] Meanwhile, the enzyme molecules diffuse into the network of the hydrogels and cause degradation. It is worth noting that the CMC/HEC hydrogel materials are degradable and expected to be applied in agriculture as a kind of coating material to alleviate the environmental pollution.

The experimental data in this study indicated that the product can effectively reduce nutrient loss and improve water use efficiency. However, to minimize the fertilizer use at the same time that food production is increased, integrated management packages need to be developed, including the evaluation of soil organic matter content, soil texture, residual soil N, good irrigation strategies, and cropping systems. In reality, achieving such a scenario represents one of the greatest scientific challenges facing humankind.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +86-931-8912387. Fax: +86-931-8912582. E-mail: mzliu@lzu.edu.cn.

Funding Sources

We gratefully acknowledge the financial support of the Special Doctorial Program Funds of the Ministry of Education of China (Grant 20090211110004) and Gansu Province Project of Science and Technologies (Grant 0804WCGA130).

REFERENCES

(1) Tilman, D.; Cassman, K. G.; Matson, P. A.; Naylor, R.; Polasky, S. Agricultural sustainability and intensive production practices. *Nature* **2002**, *418*, 671–677.

(2) Matson, P. A.; Naylor, R.; Ortiz-Monasterio, I. Integration of environmental, agronomic, and economic aspects of fertilizer management. *Science* **1998**, *280*, 112–115.

(3) Ju, X.-T.; Xing, G.-X.; Chen, X.-P.; Zhang, S.-L.; Zhang, L.-J.; Liu, X.-J.; Cui, Z.-L.; Yin, B.; Christie, P.; Zhu, Z.-L.; Zhang, F.-S. Reducing environmental risk by improving N management in intensive Chinese agricultural systems. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 3041–3046.

(4) Vitousek, P. M.; Naylor, R.; Crews, T.; David, M. B.; Drinkwater, L. E.; Holland, E.; Johnes, P. J.; Katzenberger, J.; Martinelli, L. A.; Matson, P. A.; Nziguheba, G.; Ojima, D.; Palm, C. A.; Robertson, G. P.; Sanchez, P. A.; Townsend, A. R.; Zhang, F. S. Nutrient imbalances in agricultural development. *Science* **2009**, *324*, 1519–1520.

(5) Trenkel, M. E. *Controlled-Release and Stabilized Fertilizers in Agriculture*; International Fertilizer Industry Association: Paris, France, 1997.

(6) Du, C.-w.; Zhou, J.-m.; Shaviv, A. Release characteristics of nutrients from polymer-coated compound controlled release fertilizers. *J. Polym. Environ.* **2006**, *14*, 223–230.

(7) Ibrahim, A. A.; Jibril, B. Y. Controlled release of paraffin wax/rosin-coated fertilizers. *Ind. Eng. Chem. Res.* **2005**, *44*, 2288–2291.

(8) Ni, B.; Liu, M.; Lü, S.; Xie, L.; Wang, Y. Multifunctional slow-release organic−inorganic compound fertilizer. *J. Agric. Food. Chem.* **2010**, *58*, 12373–12378.

(9) Collins, T. Toward sustainable chemistry. *Science* **2001**, *291*, 48–49.

(10) Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. Advances in cellulose ester performance and application. *Prog. Polym. Sci.* **2001**, *26*, 1605–1688.

(11) Bhardwaj, A. K.; Shainberg, I.; Goldstein, D.; Warrington, D. N.; Levy, G. J. Water retention and hydraulic conductivity of cross-linked polyacrylamides in sandy soils. *Soil Sci. Soc. Am. J.* **2007**, *71*, 406–412.

(12) Hüttermann, A.; Zommorodi, M.; Reise, K. Addition of hydrogels to soil for prolonging the survival of *Pinus halepensis* seedlings subjected to drought. *Soil Tillage Res.* **1999**, *50*, 295–304.

(13) Bakass, M.; Mokhlisse, A.; Lallemant, M. Absorption and desorption of liquid water by a superabsorbent polymer: Effect of polymer in the drying of the soil and the quality of certain plants. *J. Appl. Polym. Sci.* **2002**, *83*, 234–243.

(14) Ye, H.; Zhao, J.-Q.; Zhang, Y.-H. Novel degradable superabsorbent materials of silicate/acrylic-based polymer hybrids. *J. Appl. Polym. Sci.* **2004**, *91*, 936–940.

(15) Lü, S.; Liu, M.; Ni, B. An injectable oxidized carboxymethylcellulose/*N*-succinyl-chitosan hydrogel system for protein delivery. *Chem. Eng. J.* **2010**, *160*, 779–787.

(16) Marci, G.; Mele, G.; Palmisano, L.; Pulito, P.; Sannino, A. Environmentally sustainable production of cellulose-based superabsorbent hydrogels. *Green Chem.* **2006**, *8*, 439–444.

(17) Demitri, C.; Del Sole, R.; Scalera, F.; Sannino, A.; Vasapollo, G.; Maffezzoli, A.; Ambrosio, L.; Nicolais, L. Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. *J. Appl. Polym. Sci.* **2008**, *110*, 2453–2460.

(18) Yang, C. Q.; Wang, X. Formation of five-membered cyclic anhydride intermediates by polycarboxylic acids: Thermal analysis and Fourier transform infrared spectroscopy. *J. Appl. Polym. Sci.* **1998**, *70*, 2711–2718.

(19) Xie, X.; Liu, Q.; Cui, S. W. Studies on the granular structure of resistant starches (type 4) from normal, high amylose and waxy corn starch citrates. *Food Res. Int.* **2006**, *39*, 332–341.

(20) Coma, V.; Sebti, I.; Pardon, P.; Pichavant, F. H.; Deschamps, A. Film properties from crosslinking of cellulosic derivatives with a polyfunctional carboxylic acid. *Carbohydr. Polym.* **2003**, *51*, 265–271.

(21) Tran, C. T.; Sly, L. I.; Mitchell, D. A. Selection of a strain of *Aspergillus* for the production of citric acid from pineapple waste in solid-state fermentation. *World J. Microbiol. Biotechnol.* **1998**, *14*, 399–404.

(22) Wang, J. Improvement of citric acid production by *Aspergillus niger* with addition of phytate to beet molasses. *Bioresour. Technol.* **1998**, *65*, 243–245.

(23) Shaviv, A.; Raban, S.; Zaidel, E. Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. *Environ. Sci. Technol.* **2003**, *37*, 2251–2256.

(24) Murray, H. H. Traditional and new applications for kaolin, smectite, and palygorskite: A general overview. *Appl. Clay Sci.* **2000**, *17*, 207–221.

(25) Al-Zahrani, S. M. Controlled-release of fertilizers: Modelling and simulation. *Int. J. Eng. Sci.* **1999**, *37*, 1299–1307.

(26) Ni, B.; Liu, M. Z.; Lü, S.; Xie, L.; Zhang, X.; Wang, Y. Novel slow-release multielement compound fertilizer with hydroscopicity and moisture preservation. *Ind. Eng. Chem. Res.* **2010**, *49*, 4546–4552.

(27) Zhang, J. P.; Chen, H.; Wang, A. Q. Study on superabsorbent composite. III. Swelling behaviors of polyacrylamide/attapulgite composite based on acidified attapulgite and organo-attapulgite. *Eur. Polym. J.* **2005**, *41*, 2434–2442.

(28) Petrov, P.; Petrova, E.; Tchorbanov, B.; Tsvetanov, C. B. Synthesis of biodegradable hydroxyethylcellulose cryogels by UV irradiation. *Polymer* **2007**, *48*, 4943–4949.

(29) Bajpai, A. K.; Shrivastava, J. In vitro enzymatic degradation kinetics of polymeric blends of crosslinked starch and carboxymethyl cellulose. *Polym. Int.* **2005**, *54*, 1524–1536.