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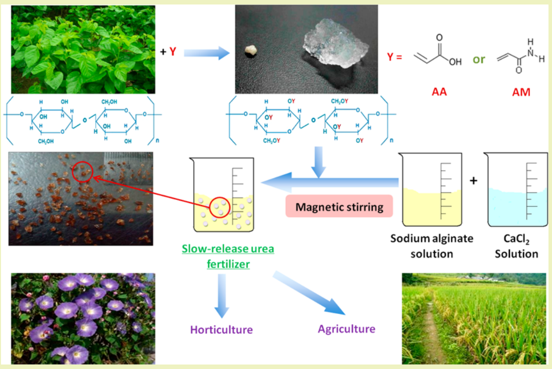
An Eco-Friendly Slow-Release Urea Fertilizer Based on Waste Mulberry Branches for Potential Agriculture and Horticulture Applications

Yong Zhang,[†,‡] Xiying Liang,[†] Xiaogang Yang,[†] Hongyi Liu,[†] and Juming Yao*,[†]

[†]The Key Laboratory of Advanced Textile Materials and Manufacturing Technology of the Ministry of Education, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, China

[‡]Zhejiang Provincial Top Key Discipline of New Materials and Process Engineering, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, China

ABSTRACT: Development of a compound fertilizer for agricultural and horticultural applications remains an important challenge in the field of biomass synthesis on account of its raw material source and biodegradability. In this work, an eco-friendly slow-release urea fertilizer (SRUF) employing mulberry branch-*g*-poly(acrylic acid-*co*-acrylamide) (MB/P(AA-*co*-AM)) superabsorbent was prepared. The MB/P(AA-*co*-AM) superabsorbent was blended with sodium alginate, urea, and $CaCl_2$ solutions to accomplish this synthesis process. The synthesis conditions of the SRUF and its application performance were examined. The results showed that under the optimal synthesis conditions the water absorbency and water absorbency rate of the SRUF reached 420.0 g/g and 60.0 (g/g)/min in deionized water, respectively. The water retention of the SRUF was 7.2 wt % after 25 d. The urea release in deionized water and soil both exhibited a typical slow release behavior. A degradation rate of 32.0 wt % was attained for the SRUF while it was buried for 90 d in soil.



KEYWORDS: *Mulberry branch, Sodium alginate, Urea slow-release, Water retention, Eco-friendly fertilizer*

INTRODUCTION

Recently, efficient utilization of agri-industrial residues has attracted substantial attention for the preparation of cellulose-based functional products, such as cellulose nanocrystals,[1] fatty acids,[2] substrate,[3] and bioethanol.[4,5] Mulberry, as an important economic crop, is widely planted all over the word.[6] But up to now, mulberry is not made full use of in many countries except for its leaves, which serve as feed sources for the silkworm industry. The rest, like branches, stems, and roots, is handled as agricultural waste for incineration or landfilling.[7] Efficient utilization of excess mulberry branches therefore remains an important challenge. Significant efforts have been dedicated to exploring the preparation and properties of mulberry branch-sourced functional materials in the past few years. Pectin,[7] cellulose whisker,[8] and natural fiber[9] were extracted from bark or xylem of mulberry branches for new materials preparation.

Water and fertilizer are two critical factors for the growth process of crops.[10] One of the methods to effectively hold water and nutrition in the soil for the crops' growing needs is the application of a superabsorbent. Recent research with encouraging results showed that a superabsorbent, which improved water irrigation and nutrient retention in soil, could act as a water and fertilizer manager in the growth of crops.[11,12] Superabsorbent, as a three-dimensionally cross-linked hydrogel, can absorb water or other liquids from tens to thousands times its weight. The absorbed liquids can also be kept in the superabsorbent under a certain pressure.[13,14] These particular advantages urge superabsorbents to be required in fields such as agriculture and horticulture,[15,16] sanitary products (such as sanitary napkins and disposable diapers),[17] environmental protection,[18] and drug delivery.[19,20]

Over the past few decades, the preparation of superabsorbents has been primarily based on synthetic polymers like acrylic acid (AA) or acrylamide (AM), which hold potential environment hazards due to their poor biodegradability.[21,22] Meanwhile, the increasingly depleted petroleum resources are their main source of raw materials. As a consequence, many efforts have been made to exploit eco-friendly raw materials for superabsorbents. Many products from renewable natural resources, such as starch,[23,24] cellulose and its derivatives,[25,26] hemicelluloses,[27,28] chitosan,[29,30] humic acid,[31] carrageenan,[32,33] and even flax yarn waste[34] have been adopted to prepare superabsorbents.

Hence, the existing problems and appropriate properties of waste mulberry branches motivate us to examine its potential applications in the field of compound fertilizers. As a continuing

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study for organic−inorganic compound superabsorbents,[35] our target focused on providing new tactics for the high-value utilization of waste mulberry branches, i.e., combining it into fertilizer for agricultural and horticultural applications. The objectives of this study were to investigate the preparation of an eco-friendly slow-release urea fertilizer (SRUF) based on mulberry branches under different synthesis conditions and to characterize the properties of the resulting fertilizer, specifically its water absorbency and retention, slow-release urea behavior, and biodegradability.

■ MATERIALS AND METHODS

Materials. Mulberry branches were reaped from the mulberry plantation of Zhejiang Sci-Tech University in Hangzhou, China. Acrylic acid (AA, analytical grade; Aladdin Chemistry Co., Ltd., China) was used after vacuum distillation. Acrylamide (AM, analytical grade; Yingguangtai Biotechology Co., Ltd., China) was employed as received. Ammonium persulfate (APS, analytical grade; TianjinYongda Chemical Co., Ltd., China) was used after recrystallization. Calcium chloride (analytical grade; Guoyao Chemical Reagent Co., Ltd., China), ammonium bicarbonate (analytical grade; Beijing Solarbio Science Technology Co., Ltd., China), *N*,*N*-methylenebis(acrylamide) (MBA, analytical grade; Guoyao Chemical Reagent Co., Ltd., China), urea (analytical grade; Beijing Solarbio Science Technology Co., Ltd., China), and sodium alginate (apparent viscosity 200−600 mPa.s, food grade; Shanghai Maichao Chemical Co., Ltd., China) were used directly. All other chemicals were of analytical grade, and solutions were formulated using deionized water.

Synthesis of MB/P(AA-*co*-AM)) Superabsorbent. *Pretreatment of Mulberry Branches.* Mulberry branches were cleaned, cut into pieces, and then dried to a constant weight at 105 °C. After smashing and screening, the pulverized mulberry branches between 100 and 200 mesh (0.072−0.143 mm) were collected. The content of cellulose in the pulverized mulberry branches was tested according to the Kurschner−Hoffer cellulose method, and the contents of hemicellulose, lignin, benzene alcohol extractives, and moisture in the pulverized mulberry branches were measured according to the TAPPI standard methods of T 223, T 244, T 204, and T 258, respectively. The main chemical components are presented in Figure 1. The cellulose content was 36.5 wt % in the used mulberry branches.

Mulberry Branches Grafted by AA and AM. The MB/P(AA-*co*-AM) superabsorbent was prepared by grafting AA and AM onto the pulverized mulberry branches by free-radical graft copolymerization according to previous research.[36] In brief, 1 g of pulverized mulberry branches was distributed in 20 mL of deionized water and then poured into a 250 mL three-necked flask with s magnetic stirrer, reflux condenser, nitrogen line, and a water bath of 70 °C. Meanwhile, oxygen-free nitrogen was introduced for 30 min before reacting, and then the APS solution (containing 0.05 g APS) was added.[34,35] After stirring for 15 min, the AA solution (containing 4.8 g AA) with a neutralization of 60%, 1.2 g of AM, and 0.02 g of MBA were added into the reaction system successively. The total volume of solution was limited at 40 mL. After 2 h, the product was washed by deionized water and ethyl alcohol in turns and then dried to a constant weight at 60 °C. The dried gel was ground into a powder and passed through a 200 mesh sieve.

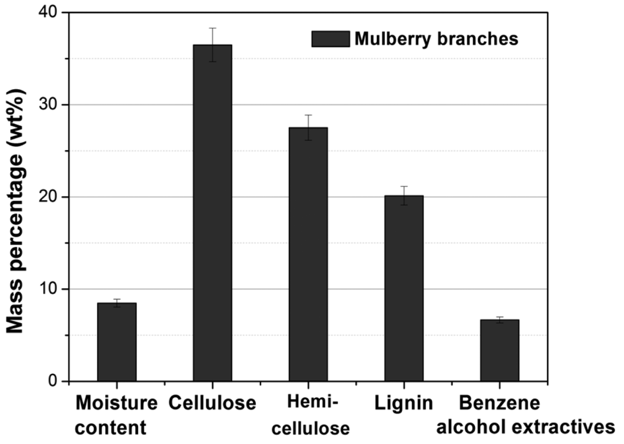

Figure 1. Main chemical components of the used mulberry branches. Data points are the means of three measurements. Error bars represent one standard deviation.

Preparation of SRUF. Sodium alginate with certain concentrations and 0.5 wt % urea aqueous solution were blended with the synthesized MB/P(AA-*co*-AM) superabsorbent (≤200 mesh). The mixed solution was added dropwise into a 0.5 wt % $CaCl_2$ solution by syringe under low-speed stirring with a injection speed of 5 mL/min. The volume ratio of the mixed solution and calcium chloride aqueous solution was 1:4. After a certain time, the calcium chloride cross-linked solution was filtered and rinsed with deionized water to remove the excess calcium chloride and then dried at 37 °C to a constant weight. Figure 2 schematically shows this proposed preparation process of the SRUF.

Properties of Prepared SRUF. *Water Absorbency.* A total of 0.1 ± 0.0001 g of SRUF powders were soaked in 500 mL of deionized water, saline solution, and tap water at 5, 25, and 45 °C, respectively, to achieve saturation. Then the swollen sample was filtered by 100 mesh nylon screen to remove unabsorbed liquids. The equilibrium swelling Q_{eq} was calculated by eq 1

$$Q_{eq} = (M_2 - M_1)/M_1 \tag{1}$$

where M_1 and M_2 are the weights of the dry and swollen samples (g), respectively, and Q_{eq} is the water absorbency of per gram dried sample (g/g).

Water Absorbency Rate. The accurately weighed SRUF powders (0.1 ± 0.0001 g) were swelled in 500 mL of deionized water. At every 0.5 min interval, the sample was fished out to measure the water absorbency. Then it was put back to the same deionized water for the next test.

Water Retention at Various Temperatures. The SRUF was soaked in deionized water at 25 °C to achieve saturation. Then the swollen SRUF was placed at 5, 25, and 45 °C, respectively. At every 1 h interval, the sample was weighed for a total period of 12 h. The water retention capacity at various temperatures R_{iT} was determined by the following equation

$$R_{iT} = M_i/M_0 \times 100\% \tag{2}$$

where M_0 and M_i are the weights of the swollen and desorbed samples (g), respectively, and R_{iT} is the water retention rate of per gram swollen sample (g/g).

Water Retention at Various Centrifugal Forces. The SRUF was soaked in deionized water at 25 °C to achieve saturation. Then the swollen SRUF was wrapped in a 200 mesh nylon screen and centrifuged with different rotation speeds for 30 min. The water retention capacity at various centrifugal forces R_i was determined by eq 3

$$R_i = (M_i - M')/(M_0 - M') \times 100\% \tag{3}$$

where M_0 and M_i are the weights of the swollen and centrifuged samples with tea bag (g), and M' is the weight of the tea bag (g). The relation between the centrifugal force (F) and rotation speed (n) was calculated by eq 4

$$F = 4\pi^2 n^2 mr \tag{4}$$

where m is the weight of the SRUF, and r is the radius of the centrifuge.

Water Retention in Soil. Soil was dried at 105 °C to constant weight and sieved with a 10 mesh nylon screen. Amounts of 0.1, 0.3, and 0.5 g of SRUF mixed with 100 gof soil powders in 500 mL glass beakers were infiltrated by running water until the water exudation from the soil gaps appeared.[37] The control experiment without the SRUF was also carried out. The beakers were placed at 25 °C and

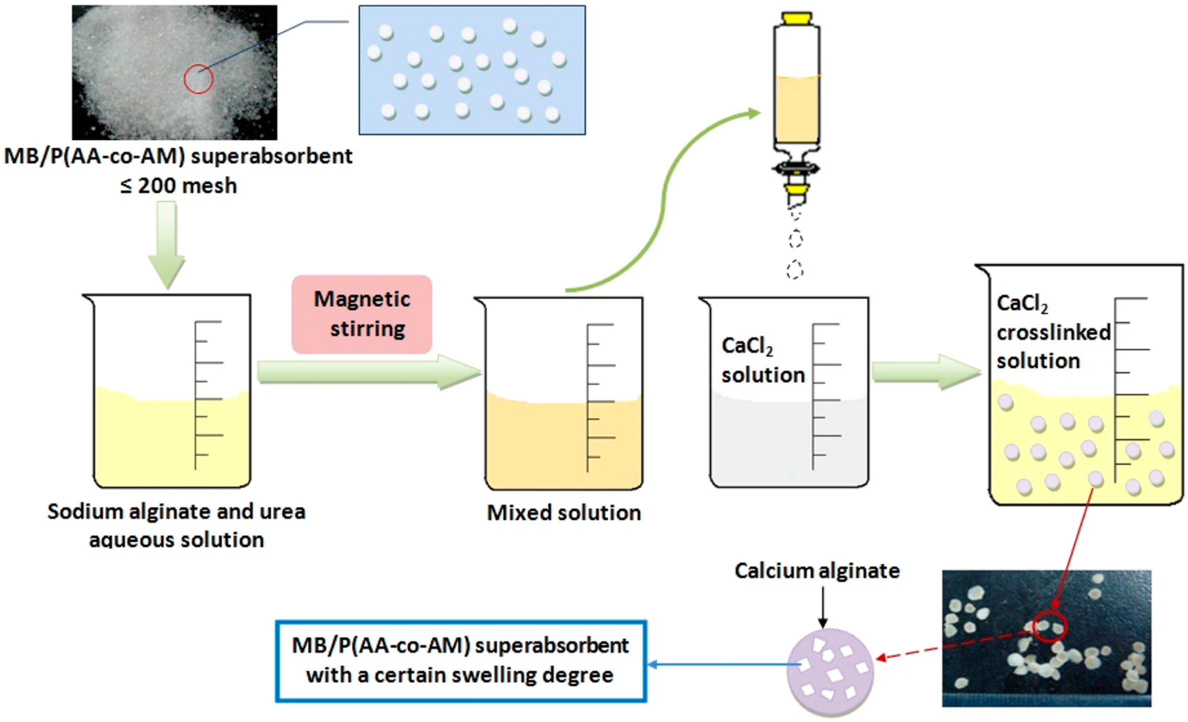

Figure 2. Proposed preparation process of the slow-release urea fertilizer.

Table 1. Factorial $L_9(3)^3$ Experiment of Syringe Caliber, $CaCl_2$ Solution, Sodium Alginate, and MB/P(AA-*co*-AM) Superabsorben[a]

sample no.	A (mm)	B (wt %)		C	Q_{eq} (g/g)	Q_{eqr} ((g/g)/min)	
1	1 (0.5)	1 (0.5)		1 (2:1)	419	63.4	
2	1 (0.5)	2 (0.7)		3 (1:2)	147	29.3	
3	1 (0.5)	3 (0.9)		2 (1:1)	154	33.0	
4	2 (2.0)	1 (0.5)		3 (1:2)	368	68.7	
5	2 (2.0)	2 (0.7)		2 (1:1)	401	56.0	
6	2 (2.0)	3 (0.9)		1 (2:1)	439	59.0	
7	3 (4.0)	1 (0.5)		2 (1:1)	348	35.7	
8	3 (4.0)	2 (0.7)		1 (2:1)	393	48.3	
9	3 (4.0)	3 (0.9)		3 (1:2)	278	41.0	
	A	B	C		A	B	C
$K_1{}^{b,d}$	252.7	378.3	417.0	$K_1{}^{b,e}$	41.9	56.0	57.0
$K_2{}^{b,d}$	402.7	313.7	313.7	$K_2{}^{b,e}$	61.2	44.5	46.3
$K_3{}^{b,d}$	339.7	303.0	264.3	$K_3{}^{b,e}$	41.7	44.3	41.6
$R^{c,d}$	150.0	75.3	152.7	$R^{c,e}$	19.6	11.6	15.3
influencing order		A > C > B A_2 B_1 C_1		influencing order		A > C > B A_2 B_1 C_1	
optimal combination				$A_2B_1C_1$			

[a] A is syringe caliber; B is concentration of $CaCl_2$ solution; C is sodium alginate to MB/P(AA-co-AM) superabsorbent mass ratio; Q_{eq} and Q_{eqr} are water absorbency and water absorbency rate in deionized water, respectively. [b] $K = (\sum$water absorbency/water absorbency rate in deionized water of single factor$)/4$. [c] $R = \max K - \min K$. [d] Water absorbency. [e] Water absorbency rate.

weighed every day for a total period of 12 d. The water retention in soil R_{is} was determined by the following equation

$$R_{is} = m_i/m_0 \quad (5)$$

where m_0 and m_i are the total weights of the saturated and desorbed samples with soil (g), respectively.

Slow-Release Urea in Water. A total of 0.2 g of SRUF was immersed in 400 mL of deionized water, which served as the release medium. At every 10 min interval, 2 mL of solution was taken out from the release medium to detect the urea content using an ultraviolet spectrophotometer method.[38] Then the same amount of fresh deionized water was supplied in the medium immediately for the next measurement. The urea cumulative release rate of the SRUF in water was calculated by eq 6

$$R_w = 400C_t + 2\sum_{i=1}^{n-1} C_i \quad (6)$$

where C_t is the urea concentration tested by ultraviolet spectrophotometer at a certain time interval (μg/mL).

Slow-Release Urea in Soil. A total of 0.3 g of SRUF was wrapped by 500 mesh nylon screen and buried in a plastic cup containing 150 g of dry soil.[39] The depth from the sample to the soil surface was 10 cm. Tap water was flowed into the plastic cup to keep moisture content of the soil at 30%. Then the plastic cup was sealed with plastic wrap. At

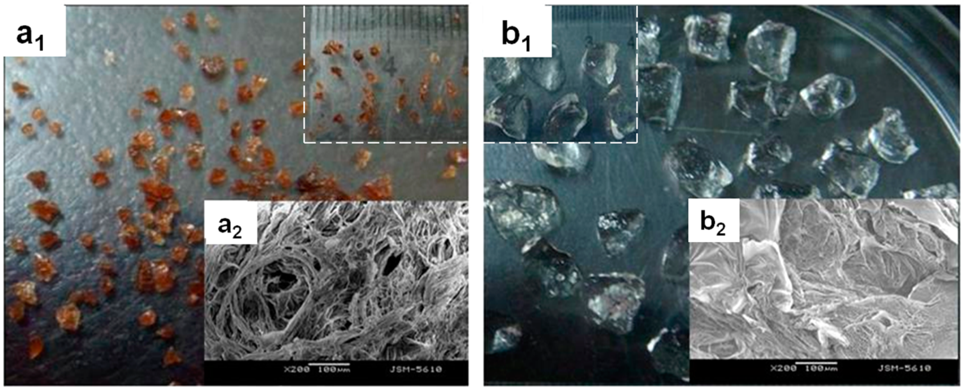

Figure 3. Actual and SEM images of the slow-release urea fertilizer formed under optimal conditions: (a_1) dried, (a_2) cross-section (magnification: × 200; scale bar: 100 μm), (b_1) saturated, (b_2) cross-section (magnification: × 200; scale bar: 100 μm).

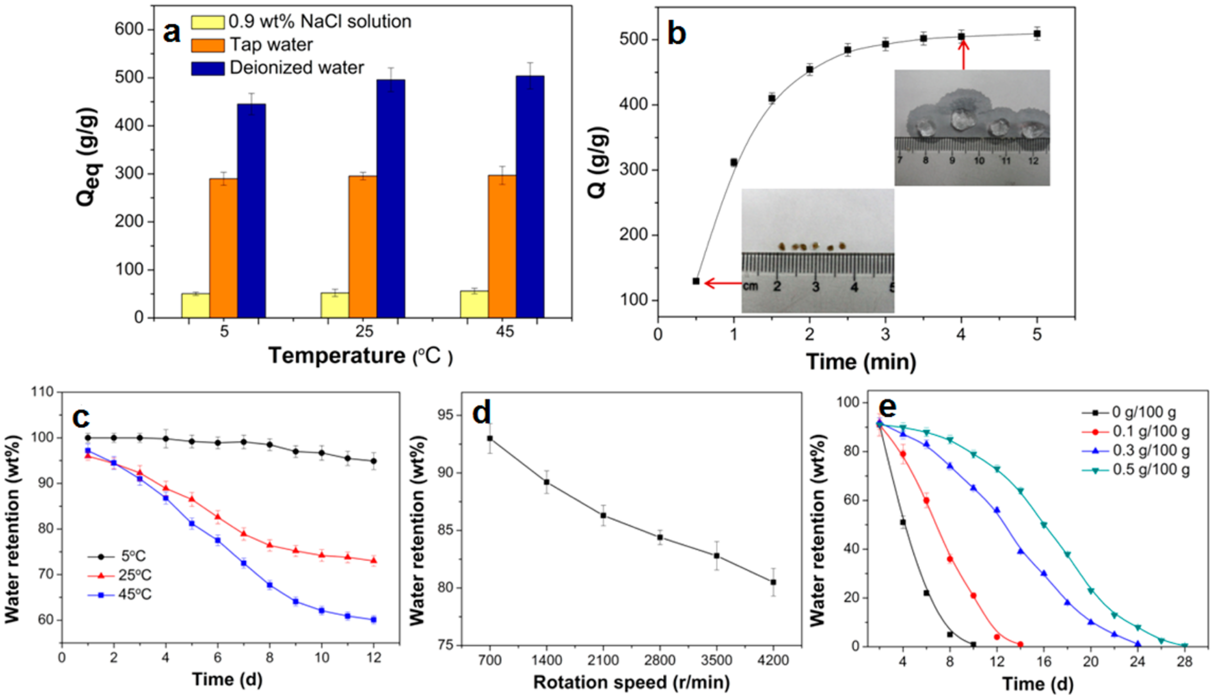

Figure 4. Water absorbency and retention of the slow-release urea fertilizer: (a) water absorbencies at different temperatures, (b) water absorbency rate in deionized water, (c) water retentions at different temperatures, (d) water retentions at various centrifugal forces,and (e) water retentions in soil with the unequal fertilizer contents. Data points are the means of three measurements. Error bars represent one standard deviation.

every 24 h interval, the sample was taken out and weighed after being dried at 37 °C to a constant weight. The weight difference method was used to calculate the urea release rate of the SRUF according to eq 7.[39] Throughout the experiment, tap water was added appropriately to maintain the moisture content of soil always about 30%.

$$R_s = (m_0 - m_s)/(m_0 - m_c) \tag{7}$$

where m_0 and m_s are the total weights of the SRUF and nylon screen before and after soil burial (g), and m_c is the total weight of the control SRUF (without loading urea) and nylon screen (g), respectively.

Natural Soil Degradation. The natural soil degradation test was carried out for 90 d. The SRUF sample was prepared with a shape of circular disk with the diameter of 10 mm and thickness of 1 mm. Then it was wrapped in a 200 mesh stainless steel wire. Each SRUF sample was buried 10 cm under the soil surface. At every 10 d interval, it was dug out. After being washed by deionized water and dried at 60 °C to constant weight, the SRUF was weighed, and its degradation rate was determined by eq 8

$$\text{Degradation \%} = (W_1 - W_2)/W_1 \times 100 \tag{8}$$

where W_1 and W_2 are the weights of the dry SRUF before and after the soil burial (g), respectively.

Morphology. The SEM images were photographed by a JSM-5610 LV SEM system using an acceleration voltage of 8 kV. The samples were sputter-coated with a gold layer in vacuum before being observed.

■ RESULTS AND DISCUSSION

Optimization of SRUF Synthesis Conditions. Sodium alginate can form an "egg-shell" structure under the action of Ca^{2+} and then achieve the task of slow-releasing the compositions wrapped in it. After blending of the MB/P(AA-*co*-AM) superabsorbent and sodium alginate in the presence of Ca^{2+}, the MB/P(AA-*co*-AM) superabsorbent was wrapped in the "egg-shell" structure of sodium alginate, which can cause a variation of the osmotic pressures inside and outside the superabsorbent and influence the water absorbency of the SRUF. Therefore, the SRUF should have an excellent water absorbing property. A factorial experiment with three factors

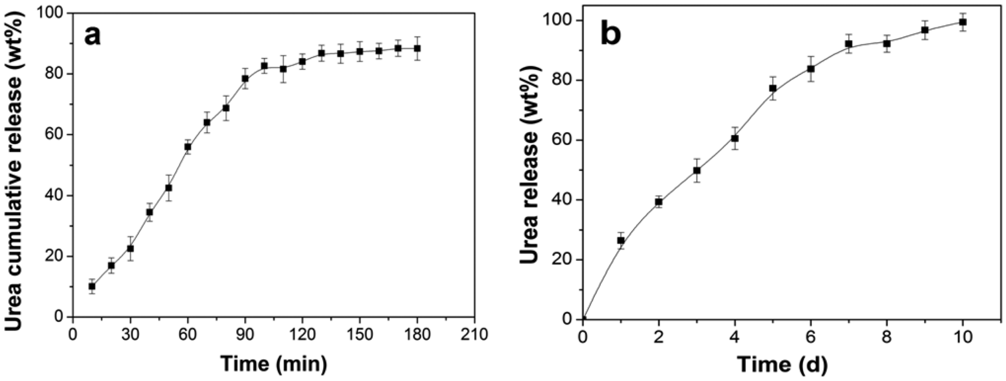

Figure 5. Slow-release urea behavior of the slow-release urea fertilizer: (a) in deionized water, (b) in soil. Data points are the means of three measurements. Error bars represent one standard deviation.

and three levels was performed to obtain the best synthesis conditions of the SRUF. "A" stands for syringe caliber, which designs three levels of 0.5, 2.0, and 4.0 mm. "B" and "C" stand for concentration of $CaCl_2$ solution and sodium alginate to MB/P(AA-*co*-AM) superabsorbent mass ratio, respectively. According to the factorial array of $L_9(3)^3$ presented in Table 1, the following experiments were carried out, and the range analysis was exhibited. It is shown that the influencing order of each factor on water absorbency and absorbency rate in deionized water is A > C > B. Syringe caliber is the most important factor, sodium alginate to MB/P(AA-*co*-AM) superabsorbent mass ratio follows, and concentration of $CaCl_2$ solution is the last. In the synthetic reaction, syringe caliber controlled the content of the MB/P(AA-*co*-AM) superabsorbent wrapped in the "egg-shell" structure of sodium alginate, which played a role in promoting the water absorbency of the SRUF. The activity of slow-release urea would also be affected, while the content of MB/P(AA-*co*-AM) superabsorbent in the "egg-shell" structure was excessive. This factor had a more significant influence than others. On the basis of the results of the factorial experiment, the optimal combination $A_2B_1C_1$ was obtained, corresponding to the optimal synthesis conditions of 2.0 mm syringe caliber, 0.5 wt % $CaCl_2$ solution, and 2:1 sodium alginate to MB/P(AA-*co*-AM) superabsorbent mass ratio. The prepared SRUF here presented the maximum water absorbency and water absorbency rate of 420.0 g/g and 60.0 (g/g)/min in deionized water, respectively. The cellulose grafting percentage and monomer graft efficiency of the MB/P(AA-*co*-AM) were 120.4 and 31.8 wt %, respectively. The total nitrogen content was 0.37 wt % in the SRUF. Figure 3 displays the actual and SEM images of the SRUF formed under the above-mentioned optimal conditions. The excellent water absorbency of the SRUF preliminarily confirmed its potential to be applied in the fields of agriculture and horticulture.

Water Absorbency and Retention of SRUF. *Water Absorbency at Various Temperatures.* The water absorbency at different temperatures is an important property for fertilizer. Figure 4a presents the water absorbency of the SRUF at 5, 25, and 45 °C, standing for the typical temperatures of soil in four seasons of temperate regions. The water absorbency of the SRUF increased slightly with the rise in temperature. The water absorbency of the SRUF appeared 445.2 g/g in deionized water, 289.7 g/g in tap water, and 50.6 g/g in 0.9 wt % aqueous NaCl solution when the temperature was 5 °C. But while the temperature increased to 25 °C, the water absorbency climbed to 495.7 g/g in deionized water, 295.4 g/g in tap water, and 52.3 g/g in 0.9 wt % aqueous NaCl solution. As the temperature reached 45 °C, it ascended to 503.9 g/g in deionized water, 296.8 g/g in tap water, and 56.1 g/g in 0.9 wt % aqueous NaCl solution. These results, which were comparable to those for wheat straw-based superabsorbent resin,[13] indicated that the water absorbency of the SRUF was stable in the same solution with the change of temperature, which exhibited the excellent performance of the SRUF both in the cold winter and hot summer.

Water Absorbency Rate in Deionized Water. As a compound fertilizer applied in agriculture and horticulture, high water absorbency rate is one of the most important properties for its efficient water absorbing and storing during raining or irrigating.[15] Figure 4b exhibits the dynamic swelling behavior of the SRUF within 5 min in deionized water. The SRUF achieved water saturation in only 3 min, and the water absorbency appeared 514.8 g/g in deionized water. The initial swelling property of the SRUF mainly depends on capillary effect and the capture of hydrophilic groups on the surface of molecular structure. When the water enters into the SRUF, it accelerates the dissociation of ionic groups. The electrostatic repulsion caused by the ionization groups procures the expansion of polymeric network, which can consequently promote more water moving into the inside structure of the SRUF.[40]

Water Retention at Various Temperatures. Water retention ability is another important property for a compound fertilizer. Figure 4c displays the water retention ability of the SRUF at 5, 25, and 45 °C. The results implied that the water retention of the SRUF decreased with the increase in temperature and time. The SRUF reserved 74.3 and 59.2 wt % of the absorbed water at 25 and 45 °C for 12 h, respectively. While at 5 °C for 12 h, 97.1 wt % of the absorbed water was preserved. The decrease in water retention with rising temperature can be explained by the fracturing of hydrogen bonds, which mainly absorb water molecules in the SRUF.[41]

Water Retention at Various Centrifugal forces. Water retention of the SRUF at various centrifugal forces was tested by centrifugal experiments under different rotation speeds. Figure 4d shows the relation between water retention and rotation speed. With the increase in rotation speed, greater pressure is generated, which led to a decrease in water retention of the SRUF. The water retention only remained at 81.5 wt % when the rotation speed rose to 4200 rpm for 30 min. The reason may be that the increasing centrifugal force breaks the links between water molecules and the hydrophilic groups in or

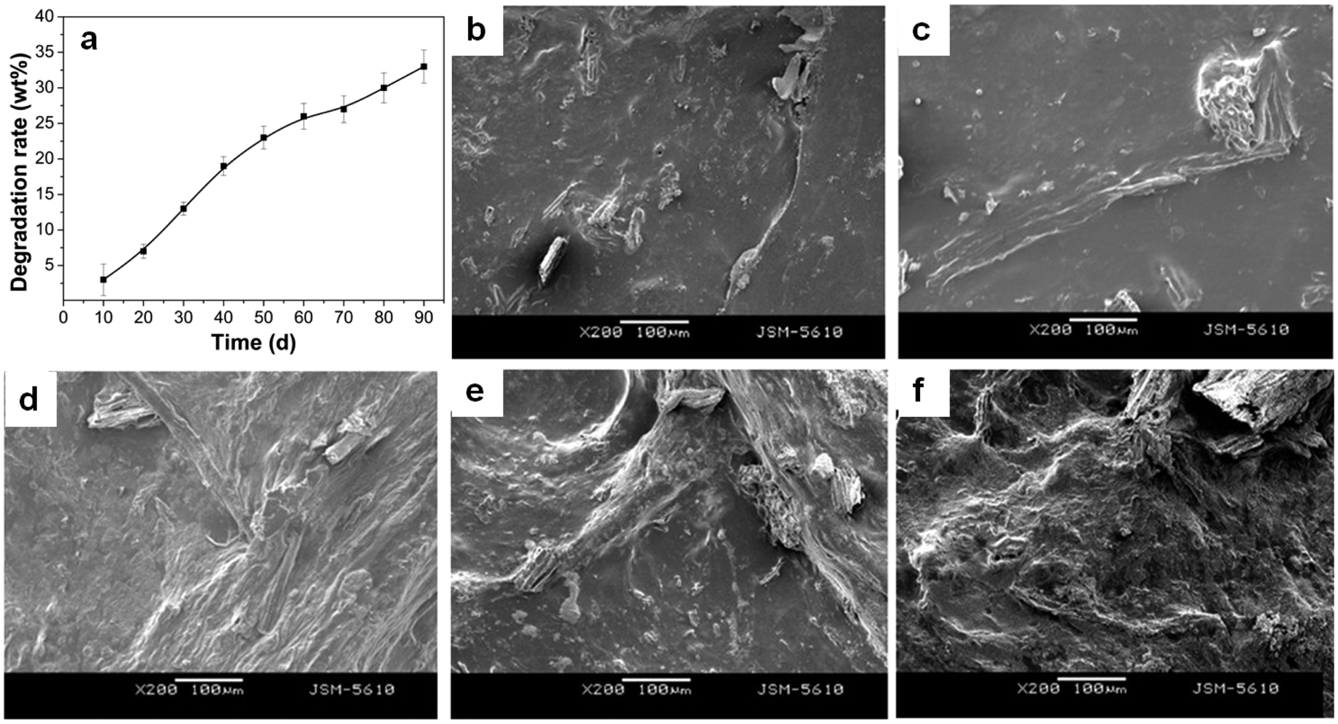

Figure 6. Degradation rate and surface morphologies of the slow-release urea fertilizer with different weight loss: (a) degradation rate, (b−f) surface morphologies of the fertilizers buried in soil after 10, 30, 50, 70, and 90 d, respectively (magnification: × 200; scale bar: 100 μm; applicable for all images.).

on the polymeric network of the SRUF. As a result, more and more water runs out.

Water Retention in Soil. Water retention in soil is one of the most important indicators for compound fertilizers used in the fields of agriculture and horticulture, which has positive effects on improving soil quality, increasing seedling survival rate, and accelerating plant growth. Figure 4e presents the water retention capacity of the SRUF in soil for 28 d. The water retention of the soil with the SRUF was significantly improved compared with that of soil without the SRUF. The water retention ratio of the control (soil without SRUF) was about 2.0 wt % after 10 d. But for the samples containing 0.1, 0.3, and 0.5 g of SRUF per 100 g of soil, the water retention ratios were, respectively, 22.4, 67.1, and 79.0 wt % after 10 d and 0.3, 40.5, and 59.7 wt % after 15 d. After 25 d, the water retention ratio of the sample with 0.5 g of SRUF per 100 g of soil still remained 7.2 wt %, which showed that the addition of the SRUF was beneficial to the improvement of water retention in soil.

Slow-Release Urea Behavior of SRUF. *Slow-Release Urea in Water.* Figure 5a shows the urea slow-release profile of the SRUF in deionized water at 25 °C. The curve exhibited a typical sustained release mode consisting of an initial slow-release followed by a plateau. The slow-release of urea lasted about 130 min. After that, the sample attained 85.2 wt % of the whole release and approached a release-adsorption balance. The "egg-shell" structure formed by calcium alginate wrapped the urea in the SRUF and made the slow-release urea behavior of the SRUF better than the poly(sodium acrylate)- or flax cellulose-based superabsorbents.[35,42] The release behavior of urea closely relies on the swelling properties of the SRUF. First, the polymer network of the SRUF extends rapidly during its fast absorbing process, leading to considerable release of urea molecules from the SRUF. Then, with the gradual saturation for the SRUF, the extension of the polymer network slowed ,and the release of urea molecules was cut back.

Slow-Release Urea in Soil. The practical application of compound fertilizer is usually buried in natural soil. Consequently, the slow-release urea behavior of the prepared SRUF in soil was measured to objectively evaluate its application prospects in agriculture and horticulture. As expected, the trend line in Figure 5b reveals that the release of urea appeared to be a classical three-stage slow-release mode: an initial high release (0−7 d), followed by a release equilibrium (7−8 d), and then a rapid release again (after 8 d). Therefore, the slow-release behavior of urea from the SRUF may be explained by the following processes: (1) With the continuous swelling of the SRUF, the urea in it dissolved rapidly. (2) When the urea was released from the SRUF, it absorbed and deabsorbed repeatedly with soil, which slowed the release rate of urea. The release and absorption between the urea and SRUF achieved balance quickly. The urea release rate stabilized. (3) With the accelerating SRUF disintegration, the urea was rapidly released again.

Biodegradability of SRUF. A soil burial test has been established and standardized for several decades. It focuses on investigating the biodegradability of material in a real soil environment. Figure 6 displays the degradation rate and surface morphologies of the SRUF with different weight losses. The degradation rates of the SRUF buried in soil after 10, 50, and 90 d were 8.2, 22.7, and 32.0 wt %, respectively, while the corresponding values of the control sample (poly(AA-*co*-AM) superabsorbent) were only 0.2, 1.9, and 3.1 wt % cited from the literature.[35] On the basis of the polymer skeleton constructed by mulberry branch cellulose, the SRUF performed an excellent biodegradability compared with the poly(AA-*co*-AM) superabsorbent. Figure 6b−f showed the different surface morphologies of the SRUF, which were buried in soil after 10, 30, 50, 70, and 90 d, respectively. Coarse and loose surfaces appeared on the soil buried samples. More and more dots and cracks emerged on the surface of the SRUF with an increase in burial time. This was mainly caused by the fracture and degradation of the mulberry cellulose macromolecular skeleton in the SRUF, which was decomposed by microorganisms and enzymes in soil.[36] In addition, mulberry branches have a low price as a kind of agri-industrial residue, in which the cellulose and hemicellulose partially replace the AA and AM in traditional superabsorbent and constitute the reticular skeleton of the SRUF. The production cost is reduced. Meanwhile, mulberry branches belong to biomass materials and have excellent biodegradability, which makes the SRUF eco-friendly. So, the resultant SRUF is considered a low-cost and eco-friendly compound fertilizer.

■ CONCLUSIONS

The objectives of this study were to investigate the preparation of an eco-friendly SRUF based on mulberry branches under different synthesis conditions and to characterize the properties of the resulting fertilizer for agricultural and horticultural applications. In light of the encouraging results, the following conclusions can be drawn. The optimal synthesis conditions of the SRUF were 2.0 mm syringe caliber, 0.5 wt % $CaCl_2$ solution, and 2:1 sodium alginate to MB/P(AA-*co*-AM) superabsorbent mass ratio. The product achieved the maximum water absorbency and water absorbency rate of 420.0 g/g and 60.0 (g/g)/min in deionized water, respectively. The water retention of the SRUF was still 7.2 wt % after 25 d. The release of urea from the SRUF in deionized water and soil both exhibited a typical slow release behavior. Finally, a degradation rate of 32.0 wt % was attained for the SRUF while it was buried for 90 d in soil. These positive results strongly suggest that as a low-cost and eco-friendly compound fertilizer, the prepared SRUF has a great potential for applications in the fields of agriculture and horticulture.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +86-571-86843618. Fax: +86-571-86843255. E-mail: yaoj@zstu.edu.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Neto, W. P. F.; Silvério, H. A.; Dantas, N. O.; Pasquini, D. Extraction and characterization of cellulose nanocrystals from agro-industrial residue – Soy hulls. *Ind. Crops Prod.* **2013**, *42*, 480–488.

(2) Scoma, A.; Bertin, L.; Fava, F. Effect of hydraulic retention time on biohydrogen and volatile fatty acids production during acidogenic digestion of dephenolized olive mill wastewaters. *Biomass. Bioenergy* **2013**, *48*, 51–58.

(3) Sugumaran, K. R.; Kumar, B. K.; Mahalakshmi, M.; Ponnusami, V. Cassava bagasse – Low cost substrate for thermotolerant xylanase production using *Bacillus subtilis*. *Int. J. ChemTech Res.* **2013**, *5*, 394–400.

(4) Konar, E. M.; Harde, S. M.; Kagliwal, L. D.; Singhal, R. S. Value-added bioethanol from spent ginger obtained after oleoresin extraction. *Ind. Crops Prod.* **2013**, *42*, 299–307.

(5) Singh, A.; Bishnoi, N. R. Comparative study of various pretreatment techniques for ethanol production from water hyacinth. *Ind. Crops Prod.* **2013**, *44*, 283–289.

(6) Wasano, N.; Konno, K.; Nakamura, M.; Hirayama, C.; Hattori, M.; Tateishi, K. A unique latex protein, MLX56, defends mulberry trees from insects. *Phytochemistry* **2009**, *70*, 880–888.

(7) Liu, L.; Cao, J.; Huang, J.; Cai, Y. R.; Yao, J. M. Extraction of pectins with different degrees of esterification from mulberry branch bark. *Bioresour. Technol.* **2010**, *101*, 3268–3273.

(8) Li, R. J.; Fei, J. M.; Cai, Y. R.; Li, Y. F.; Feng, J. Q.; Yao, J. M. Cellulose whiskers extracted from mulberry: A novel biomass production. *Carbohydr. Polym.* **2009**, *76*, 94–99.

(9) García, R.; Pizarro, C.; Lavín, A. G.; Bueno, J. L. Characterization of Spanish biomass wastes for energy use. *Bioresour. Technol.* **2012**, *103*, 249–258.

(10) Sorour, M.; EI-Sayed, M.; Moneem, N. A. E.; Talaat, H. A.; Shalaan, H.; Marsafy, S. E. Characterization of hydrogel synthesized from natural polysaccharides blend grafted acrylamide using microwave (MW) and ultraviolet (UV) techniques. *Starch – Stärke* **2013**, *65*, 172–178.

(11) Guilherme, M. R.; Oliveira, R. S.; Mauricio, M. R.; Cellet, T. S. P.; Pereira, G. M.; Kunita, M. H.; Muniz, E. C.; Rubira, A. F. Albumin release from a brain-resembling superabsorbent magnetic hydrogel based on starch. *Soft Matter* **2012**, *8*, 6629–6637.

(12) Zhu, H.; Yao, X. Synthesis and characterization of poly(acrylamide-co-2-acrylamido-2-methylpropane sulfonic acid)/kaolin superabsorbent composite. *J. Macromol. Sci., Part A: Pure Appl.Chem.* **2013**, *50*, 175–184.

(13) Ma, Z. H.; Li, Q.; Yue, Q. Y.; Gao, B. Y.; Xu, X.; Zhong, Q. Q. Synthesis and characterization of a novel super-absorbent based on wheat straw. *Bioresour. Technol.* **2011**, *102*, 2853–2858.

(14) Nair, S. S.; Zhu, J. Y.; Deng, Y. L.; Ragauskas, A. J. Hydrogels prepared from cross-linked nanofibrillated cellulose. *ACS Sustainable Chem. Eng.* **2014**, *2*, 772–780.

(15) Wu, L.; Liu, M. Z. Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention. *Polym. Adv. Technol.* **2008**, *19*, 785–792.

(16) Islam, R. M.; Hu, Y. G.; Mao, S. S.; Mao, J. Z.; Eneji, A. E.; Xue, X. Z. Effectiveness of a water-saving super-absorbent polymer in soil water conservation for corn (*Zea mays* L.) based on eco-physiological parameters. *J. Sci. Food. Agric.* **2011**, *91*, 1998–2005.

(17) Kosemund, K.; Schlatter, H.; Ochsenhirt, J. L.; Krause, E. L.; Marsman, D. S.; Erasala, G. N. Safety evaluation of superabsorbent baby diapers. *Regul. Toxicol. Pharmacol.* **2009**, *53*, 81–89.

(18) Shukla, N. B.; Rattan, S.; Madras, G. Swelling and dye-adsorption characteristics of an amphoteric superabsorbent polymer. *Ind. Eng. Chem. Res.* **2012**, *51*, 14941–14948.

(19) Wu, D. Q.; Wang, T.; Lu, B.; Xu, X. D.; Cheng, S. X.; Jiang, X. J.; Zhang, X. Z.; Zhou, R. X. Fabrication of supramolecular hydrogels for drug delivery and stem cell encapsulation. *Langmuir* **2008**, *24*, 10306–10312.

(20) Mahdavinia, G. R.; Pourjavadi, A.; Hosseinzadeh, H.; Zohuriaan, M. J. Modified chitosan 4. superabsorbent hydrogels from poly(acrylic acid-co-acrylamide) grafted chitosan with salt- and pH responsiveness properties. *Eur. Polym. J.* **2004**, *40*, 1399–1407.

(21) Wang, J.; Wang, A. Synthesis, characterization and swelling behaviors of hydroxyethyl cellulose-g-poly(acrylic acid)/attapulgite superabsorbent composite. *Polym. Eng. Sci.* **2010**, *50*, 1019–1027.

(22) Zohuriaan-Mehr, M. J.; Kabiri, K. Superabsorbent polymer materials: A review. *Iran. Polym. J.* **2008**, *17*, 451–477.

(23) Li, A.; Zhang, J. P.; Wang, A. Q. Utilization of starch and clay for the preparation of superabsorbent composite. *Bioresour. Technol.* **2007**, *98*, 119–122.

(24) Peng, G.; Xu, S. M.; Peng, Y.; Wang, J. D.; Zheng, L. C. A new amphoteric superabsorbent hydrogel based on sodium starch sulfate. *Bioresour. Technol.* **2008**, *99*, 444−447.

(25) Dahou, W.; Ghemati, D.; Oudia, A.; Aliouche, D. Preparation and biological characterization of cellulose graft copolymers. *Biochem. Eng. J.* **2010**, *48*, 187−194.

(26) Chen, L.; Berry, R. M.; Tam, K. C. Synthesis of β-cyclodextrin-modified cellulose nanocrystals (CNCs)@Fe_3O_4@SiO_2 superparamagnetic nanorod. *ACS Sustainable Chem. Eng.* **2014**, *2*, 951−958.

(27) Peng, X. W.; Ren, J. L.; Zhong, L. X.; Peng, F.; Sun, R. C. Xylan-rich hemicelluloses-graft-acrylic acid ionic hydrogels with rapid responses to ph, salt and organic solvents. *J. Agric. Food Chem.* **2011**, *59*, 8208−8215.

(28) Peng, X. W.; Zhong, L. X.; Ren, J. L.; Sun, R. C. Highly effective adsorption of heavy metal ions from aqueous solutions by macroporous xylan-rich hemicelluloses-based hydrogel. *J. Agric. Food Chem.* **2012**, *60*, 3909−3916.

(29) Ge, H. C.; Pang, W.; Luo, D. K. Graft copolymerization of chitosan with acrylic acid under microwave irradiation and its water absorbency. *Carbohydr. Polym.* **2006**, *66*, 372−378.

(30) Wu, D.; Wang, T.; Lu, B.; Xu, X. D.; Cheng, S. X.; Jiang, X. J.; Zhang, X. Z.; Zhou, R. X. Fabrication of supramolecular hydrogels for drug delivery and stem cell encapsulation. *Langmuir* **2008**, *24*, 10306−10312.

(31) Chu, M.; Zhu, S. Q.; Li, H. M.; Huang, Z. B.; Li, S. Q. Synthesis of poly(acrylic acid)/sodium humate superabsorbent composite for agricultural use. *J. Appl. Polym. Sci.* **2006**, *102*, 5137−5143.

(32) Pourjavadi, A.; Amini-Fazl, M. S. Optimized synthesis of carrageenan-graft-poly(sodium acrylate) superabsorbent hydrogel using the Taguchi method and investigation of its metal ion absorption. *Polym. Int.* **2007**, *56*, 283−289.

(33) Salimi, H.; Pourjavadi, A.; Seidi, F.; Jahromi, P. E.; Soleyman, R. New smart carrageenan-based superabsorbent hydrogel hybrid: Investigation of swelling rate and environmental responsiveness. *J. Appl. Polym. Sci.* **2010**, *117*, 3228−3238.

(34) Wu, F.; Zhang, Y.; Liu, L.; Yao, J. M. Synthesis and characterization of a novel cellulose-g-poly(acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste. *Carbohydr. Polym.* **2012**, *87*, 2519−2525.

(35) Zhang, Y.; Wu, F.; Liu, L.; Yao, J. M. Synthesis and urea sustained-release behavior of an eco-friendly superabsorbent based on flax yarn wastes. *Carbohydr. Polym.* **2013**, *91*, 277−283.

(36) Liang, X. Y.; Zhang, Y.; Liu, L.; Yao, J. M. Synthesis and urea-Loading of an eco-friendly superabsorbent composite based on mulberry branches. *Bioresources* **2013**, *8*, 130−144.

(37) Xie, J. J.; Han, X. Q.; He, X. J. Water retention capacity of soil for high absorbing water resin of PAAM. *J. Mater. Eng.* **2010**, *3*, 84−88.

(38) Watt, G. W.; Chrisp, J. D. Spectrophotometric method for determination of urea. *Anal. Chem.* **1954**, *26*, 452−453.

(39) Liang, R.; Liu, M. Z. Preparation and properties of a double-coated slow-release and water-retention urea fertilizer. *J. Agric. Food Chem.* **2006**, *54*, 1392−1398.

(40) Li, Q.; Ma, Z. H.; Yue, Q. Y.; Gao, B. Y.; Li, W. H.; Xu, X. Synthesis, characterization and swelling behavior of superabsorbent wheat straw graft copolymers. *Bioresour. Technol.* **2012**, *118*, 204−209.

(41) Roy, A.; Bajpai, J.; Bajpai, A. K. Dynamics of controlled release of chlorpyrifos from swelling and eroding biopolymeric microspheres of calcium alginate and starch. *Carbohydr. Polym.* **2009**, *76*, 222−231.

(42) Zheng, T.; Liang, Y. H.; Ye, S. H.; He, Z. Y. Superabsorbent hydrogels as carriers for the controlled-release of urea: Experiments and a mathematical model describing the release rate. *Biosyst. Eng.* **2009**, *102*, 44−50.