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# Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention

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#### **Abstract**

To improve the utilization of fertilizer and water resource at the same time, a new type chitosan-coated nitrogen, phosphorus and potassium compound fertilizer with controlled-release and water-retention (CFCW) was prepared, which possessed the three-layer structure. Its core was water-soluble nitrogen, phosphorus and potassium (NPK) fertilizer granular, the inner coating was chitosan (CTS), and the outer coating was poly(acrylic acid-co-acrylamide) (P(AA-co-AM)) superabsorbent polymer. Atomic absorption spectrophotometer and element analysis results showed that the product contained 7.98% potassium (shown by  $K_2O$ ), 8.14% phosphorus (shown by  $P_2O_5$ ), and 8.06% nitrogen. The synthesis conditions of inversion suspension polymerization were studied systematically. The water absorbency of the product was 70 times its own weight if it was allowed to swell in tap water at room temperature for 90 min. The nutrients slow release behaviors of the CFCW in soil and water-retention capacity of the soil with CFCW were investigated. A possible slow release mechanism was proposed and the release rate factor K and the release exponent n of nutrients in CFCW was calculated. This product with good controlled-release and water-retention capacity, being degradable in soil and environment-friendly, could be especially useful in agricultural and horticultural applications.

Keywords: Chitosan; P(AA-co-AM) superabsorbent; Controlled-release; Water-retention; NPK compound fertilizer

# 1. Introduction

The growth of plants and their quality are mainly a function of the quantity of fertilizer and water. So it is very important to improve the utilization of water resources and fertilizer nutrients. However, about 40–70% of nitrogen, 80–90% of phosphorus, and 50–70% of potassium of the applied normal fertilizers is lost to the environment and cannot be absorbed by plants, which causes not only large economic and resource losses but also very serious environmental pollution. Recently, the use of slow release fertilizers is a new trend to save fertilizer consumption and to minimize environmental pollution (Akelah, 1996; Jarosiewicz & Tomaszewska, 2003).

Slow release fertilizers are made to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant. These fertilizers can be physically prepared by coating granules of conventional fertilizers with various materials that reduce their dissolution rate. The release and dissolution rates of water-soluble fertilizers depend on the coating materials. At present, coating material's degradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues (Ge et al., 2002; Shavit, Reiss, & Shaviv, 2002).

Chitosan is a highly deacetylated derivative of chitin, one of the most abundant natural and biodegradable polymers. It has been widely applied in the biomedical, pharmaceutical, and agricultural fields. In many of these applications chitosan is extremely attractive due to its biodegradability, biocompatibility, and nontoxicity (Huacai, Wan, & Dengke, 2006). Therefore, the soluble fertilizer

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coated by carbohydrate polymers, such as chitosan, would be an ideal slow release formulation.

Superabsorbents are loosely crosslinked hydrophilic polymers that can absorb and retain aqueous fluids up to thousands of times their own weight, and the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, superabsorbent polymers had been widely used in agriculture and horticulture (Zhang, Li, & Wang, 2006). Recently, research on the use of superabsorbent polymers as water managing materials for the renewal of arid and desert environment has attracted great attention, and encouraging results have been observed as they can reduce irrigation water consumption, and lower the death rate of plants (Bajpai & Giri, 2003; Lin, Wu, Yang, & Pu, 2001). The optimized combination of slow release fertilizers and superabsorbent polymers may improve the nutrition of plants, mitigate the environmental impact from water-soluble fertilizers, reduce water evaporation losses, and lower the frequency of irrigation.

On the basis of the above background and our previous studies on superabsorbent polymers (Chen, Liu, & Ma, 2005; Qi, Liu, Chen, & Liang, 2007) and slow release fertilizers (Guo, Liu, Zhan, & Wu, 2005; Liang & Liu, 2006), we prepared in this study chitosan-coated NPK compound fertilizer with controlled-release and water-retention (CFCW), whose inner coating was chitosan (CTS), and the outer coating was poly(acrylic acid-co-acrylamide) (P(AA-co-AM)) superabsorbent polymer. The product we prepared not only has controlled-release property but also could absorb water and preserve the soil moisture at the same time. These were significant advantages over the normal slow release fertilizers and superabsorbent polymers for agriculture, which general have only a controlledrelease property or water-retention function. In addition, the chitosan in the first layer of the coating material was a biodegradable material and the copolymer of AA and AM of the outer coating material can also be degraded in soil, so the coating materials were not harmful to the soil. The aim of the present work is to reveal the synthesis conditions of inversion suspension polymerization, controlledrelease, and water-retention properties of the CFCW.

### 2. Experimental

### 2.1. Materials

Chitosan (CTS, degree of deacetylation is 0.9, average molecular weight is  $6.0 \times 10^5$ ) was kindly provided by Jinxing Biochemical Co (Zhejiang, China). Acrylic acid (AA, distilled under reduced pressure before use) was supplied by Beijing Eastern Chemical Works (Beijing, China). Acrylamide (AM), ammonium persulfate (APS, recrystallized from distilled water before use) and N,N'-methylenebisacrylamide (NNMBA, used as received) were supplied by Shanghai Chemical Reagent Factory (Shanghai, China). NPK compound fertilizer was industrial grade.

### 2.2. Preparation of CFCW

NPK compound fertilizer granule, previously sieved to about 2 mm in diameter was placed into a rotary drum, and the CTS powder was stuck on the granules by means of epoxy dissolved in acetone. The adhesive was applied by spraying at regular time intervals. The process was finished until compact and homogeneous coating formed on fertilizer granule. The coated granules were dried to a constant mass at room temperature for 8 h. Then the CTS-coated NPK compound fertilizer granules were obtained.

The CTS-coated NPK compound fertilizer granules (5 g) were added into a flask equipped with a mechanical stirrer, a condenser, and a drop funnel. A certain amount of carbon tetrachloride, polyethylene glycoloctyl phenyl ether (OP), and sorbite anhydride monostearic acid ester (Span-80) were added into the flask. The temperature was raised to 65 °C using a water bath while the contents were constantly stirred. After that, a certain amount of mixed solution of partially neutralized acrylic acid (AA, by N,N'-methylenebisacrylamide ammonia). acrylamide, (NNMBA) solution, and ammonium persulfate (APS) solution was slowly dropped into the flask. The mixture was filtered to remove the carbon tetrachloride after being stirred for 2 h at 65 °C and then dried in a 70 °C oven to obtain the final product, chitosan-coated NPK compound fertilizer with controlled-release and water-retention (CFCW).

### 2.3. Component and structural analysis of CFCW

Contents of nitrogen, phosphorus, and potassium in the CFCW were determined by an element analysis instrument (Germany Elemental Vario EL Crop., model 1106) and atomic absorption spectrophotometer (American TJA Crop., model 1100-B). The structure of CFCW was 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 sample was metal coated with a layer of gold and observed in a JSM-5600LV SEM manufactured in Japan.

# 2.4. Characterization of the outer coating material of CFCW by FTIR

The outer coating material of CFCW, P(AA-co-AM) was characterized by a Fourier Transform Infrared (FTIR) spectrophotometer (American Nicolet crop., model 170-SX).

# 2.5. Measurement of water absorbency of CFCW

A sample (1 g) of the CFCW was immersed into a certain amount of tap water and allowed to soak at room temperature for 90 min. The swollen CFCW was filtrated through an 80-mesh sieve to remove non-absorbed water and weighted. The water absorbency was calculated using the following equation:

$$WA = \frac{M - M_0}{M_0} \tag{1}$$

Here M and  $M_0$  denote the weight of swollen CFCW and the weight of the dry CFCW, respectively, and WA is the water absorbency per gram of dried CFCW.

### 2.6. Slow release behavior of CFCW in soil

To study the slow release behavior of CFCW in soil, the following experiment was carried out: 1 g of CFCW was well mixed with 200 g of dry soil (below 26-mesh) and kept in a 200 ml 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 necessarv. periodically. After 1, 3, 5, 10, 15, 20, 25 and 30 days incubation period, the remaining granular CFCW in the beakers were picked out and washed with distilled water, and then dried at room temperature overnight to estimate the contents of N, P and K. For eight measurements, eight beakers were prepared at the same time. The remaining amount of N, P and K was estimated by the Kieldahl method of distillation (Abraham & Rajasekharan, 1996) and atomic absorption spectrophotometer, respectively.

The release results were analyzed by using an empirical equation to estimate the value of n and K as follows (Al-Zahrani, 1999; Peng, Zhang, & Kennedy, 2006):

$$\frac{M_t}{M} = Kt^n$$
 or  $\log\left(\frac{M_t}{M}\right) = \log(K) + n\log(t)$  (2)

where  $M_t/M$  is the released fraction at time t, n is the release exponent, and K is the release factor. From the slope and intercept of the plot of  $\log(M_t/M)$  versus  $\log(t)$ , kinetic parameters n and K were calculated.

## 2.7. 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 semi-desert region. A 2 g sample of CFCW was well mixed with 200 g of dry soil (below 26-mesh) and placed in a PVC tube of 4.5 cm diameter; the bottom of the tube was sealed by nylon fabric (with an aperture of 0.076 mm) and weighed  $(W_1)$ . The soil samples were slowly drenched by tap water from the top of the tube until the water seeped out from the bottom. After there was no seeping water at the bottom, the tube was weighed again  $(W_2)$ . A control experiment, viz., with no CFCW, was also carried out. The largest water-holding ratio  $(W_2)$ 0 of the soil was calculated using the following equation:

$$W\% = \frac{100 \times (W_2 - W_1)}{W_2 - W_1 + 200} \tag{3}$$

# 2.8. Measurement of the water retention of CFCW in soil

Two grams of CFCW was well mixed with 200 g of dry sandy soil (below 2 mm in diameter) and kept in a beaker and then 200 g of tap water was slowly added into the beaker and weighed  $(W_1)$ . A controlled experiment, i.e., without CFCW, was also carried out. The beakers were maintained at room temperature and were weighed every 4 days  $(W_i)$  over a period of 28 days. The water retention ratio (WR%) of soil was calculated using the following equation:

$$WR\% = \frac{W_i}{W_1} \tag{4}$$

#### 3. Results and discussion

### 3.1. The structure and characteristics of CFCW

The structure of CFCW fertilizer granule was the three-layer, which the core is NPK compound fertilizer (52.8 wt%), the inner coating is CTS (12.3 wt%) and the outer coating is P(AA-co-AM) superabsorbent polymer (34.9 wt%), respectively (see Fig. 1). Element analysis and atomic absorption spectrophotometer results showed that N, P, and K contents of CFCW were 8.06, 8.14% (shown by P<sub>2</sub>O<sub>5</sub>), and 7.98% (shown by K<sub>2</sub>O) wt%. The average weight of the CFCW fertilizer granules was 0.26 g. The average diameters of dry CFCW and swollen CFCW granules in tap water were 2.3 and 12.4 mm, respectively.

# 3.2. FTIR analysis of P(AA-co-AM) (the outer coating material)

The infrared spectrum of P(AA-co-AM) shows in Fig. 2. The observed peaks are at  $3439~\text{cm}^{-1}$ , corresponding to N–H stretching of acrylamide unit,  $2925~\text{cm}^{-1}$ , corresponding to the C–H stretching of acrylate unit,  $1701~\text{cm}^{-1}$ , corresponding to the stretching of C=O in acrylate unit,  $1635~\text{cm}^{-1}$ , corresponding to the carbonyl moiety of the acrylamide unit,  $1075~\text{cm}^{-1}$ , corresponding to the –CO–O–stretching of acrylate unit. These results proved that the outer coating was P(AA-co-AM) superabsorbent polymer.

### 3.3. Influence of the parameters on water absorbency

The key properties of superabsorbent polymers are the water absorbency and the elastic modulus of the swollen crosslinked gel, both of which are related to the crosslinking density of the network. To improve the water absorbency capacity of the CFCW, various reaction parameters are employed. The complete details of the influence of the reaction parameters on water absorbency in tap water, such as the content of AM, crosslinking agent, initiator, neutralization degree, are given below.

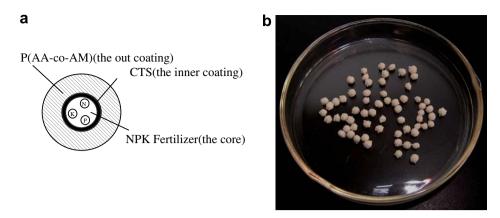


Fig. 1. The cross-section schematic view (a) and photograph (b) of CFCW fertilizer granule.

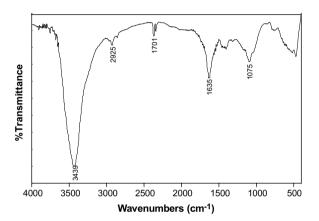


Fig. 2. The FTIR spectrum of P(AA-co-AM).

# 3.3.1. Effect of the amount of AM on water absorbency

Hydrophilic group plays an extremely important part in water absorbency. In the P(AA-co-AM) polymeric system, the ratio of different hydrophilic groups can be adjusted by changing the proportion of AA-AM. The effect of the amount of AM on water absorbency of CFCW is shown

in Fig. 3. The water absorbency increases as the amount of AM rise from 10 to 20 wt% and decreases when the amount of AM is greater than 20 wt%. It is known that AM is a nonionic monomer. It almost does not ionize in solution, so the ions in solution have little influence on it. which would improve the salt-resistance ability of CFCW. Therefore, with the increase of the amount of AM, water absorbency would increase with that. On the other hand, -COO group has better hydrophilic ability than -CONH<sub>2</sub>, so water absorbency would decrease with the further increase of the amount of AM. In other words, the maximum in the dependence of water absorbency on the amount of AM could be attributed to the cooperation effect between the salt-resistance property of the -CONH<sub>2</sub> group and the high hydrophilic ability of the -COOgroup.

3.3.2. Effect of the amount of initiator on water absorbency Fig. 4 shows the effect of the amount of initiator on water absorbency of CFCW. The water absorbency increases as the amount of initiator rise from 0.45 to

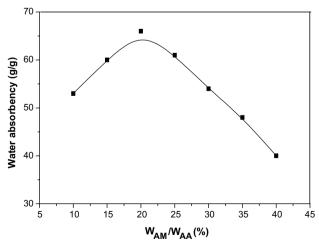


Fig. 3. The effect of the amount of AM on water absorbency. Neutralization degree, 70%; initiator, 0.91 wt%; crosslinking agent, 0.28 wt%; reaction temperature, 65  $^{\circ}$ C.

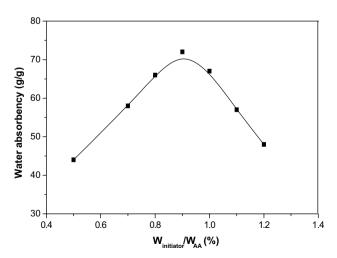


Fig. 4. The effect of the amount of initiator on water absorbency. AM, 20 wt%; neutralization degree, 70%; crosslinking agent, 0.28 wt%; reaction temperature, 65  $^{\circ}$ C.

0.91 wt% and decreases when the amount of initiator is greater than 0.91 wt%. According to the theory of Flory (Flory, 1953), the molecular weight in free radical polymerization will decrease with an increase of initiator concentration. With the decrease of the molecular weight, the relative amount of polymer chain ends increases. As reported in a previous study (Kiatkamjornwong & Wongwatthaasatien, 2004), the polymer chain ends do not contribute to the water absorbency. Therefore, the increase of the amount of initiator is responsible for the decrease in water absorbency. However, further decreases in the amount of initiator below the optimum values are accompanied by a decrease in water absorbency. This result may be attributed to a decrease in the number of radicals produced as the amount of initiator decreases. The network cannot form efficiently with a small number of radicals in the free radical polymerization that result in the decrease of the water absorbency.

# 3.3.3. Effect of the amount of crosslinking agent on water absorbency

The crosslinking agent plays an important role in the formation of three-dimensional network structures permanently in the polymerization process. This is also a promising factor directly affecting the water absorbency of CFCW. Fig. 5 shows the water absorbency in tap water as a function of the amount of crosslinking agent. It can be found that there exists a maximum, and the highest water absorbency occurs at 0.28 wt% crosslinking agent. When the crosslinking agent is lower than 0.28 wt%, the water absorbencies decrease because of the increase of soluble materials. On the other hand, higher crosslinking agent results in the generation of more crosslink points, which in turn cause the formation of an additional network and decrease the space for holding water. These results are in conformity with the theory of Flory (Flory, 1953).

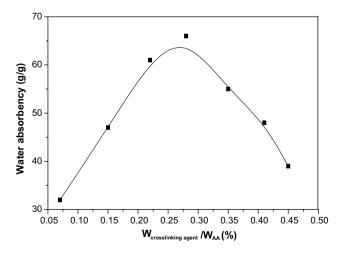


Fig. 5. The effect of the amount of crosslinking agent on water absorbency. AM, 20 wt%; neutralization degree, 70%; initiator, 0.91 wt%; reaction temperature, 65 °C.

# 3.3.4. Effect of neutralization degree of AA on water absorbency

The neutralization degree of AA dependence of water absorbency of CFCW is presented in Fig. 6. Neutralization degree is defined as the molar percentage of carboxyls in AA neutralized by ammonia. It can be found that there exists a maximum and the highest water absorbency occurs at neutralization degree = 70%. It was expected that the activity of acrylic acid is higher than acrylate, when the neutralization degree was lower than 70%, the lower neutralization degree was faster than the rate of the polymerization, the content of the oligomers would increase, and the content of acrylate would decrease, so the soluble part increased and the electrostatic repulsion between the attached carboxylate anions decreased, so that the stretching extend of hydrogel network decreased, and this resulted in water absorbency increasing with the increase of neutralization degree. It was expected that the activity of acrylic acid is higher than acrylate so the lower the neutralization degree was, the faster the polymerization rate was, and the high polymerization rate would result the increase of the content of oligomers (the soluble part) in CFCW. At the same time, the charge density of the network would increase with the increase of neutralization degree, and this would result the increase of the stretching extend of the hydrogel network, so it is easy to understand the increase of water absorbency as the neutralization degree increased from 0 to 70%.

## 3.4. Slow release behavior of CFCW

One of the most important characteristics of CFCW we prepared was its controlled-release property. Fig. 7 represents the N, P and K slow release behaviors of CFCW in soil. It could be seen from Fig. 7 that the N, P, and K in CFCW released 14.7, 10.9 and 12.4% on the 3rd days, 19.2, 14.3 and 16.7% on the 5th days, and 79, 62, and

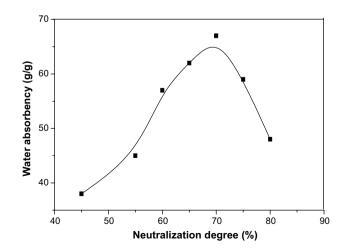


Fig. 6. The effect of neutralization degree of AA on water absorbency. AM, 20 wt%; initiator, 0.91 wt%; crosslinking agent, 0.28 wt%; reaction temperature, 65 °C.

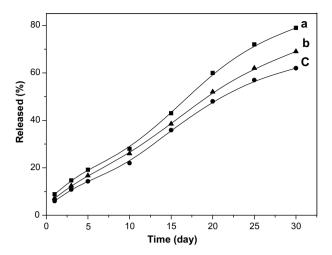


Fig. 7. Release behaviors of nitrogen (a), potassium (b), and phosphorus (c) in soil.

69% on the 30th days, respectively. With the sum of nutrients release lower than 15% on the 3rd day and not above 75% on the 30th day, this indicated that the slow release character of the CFCW we prepared agreed with the standard of slow release fertilizers of the Committee of European Normalization (CEN) (Trenkel, 1997), and also indicated that the CFCW had an excellent controlled-release property.

The nutrient release mechanism of CFCW in soil can be described by the following steps: (1) The outer P(AA-co-AM) layer is slowly swollen by the water in soil and transforms to hydrogel. A dynamic exchange between the free water in the hydrogel and the water in soil will develop (David & Mark, 1994; Smyth, Francis, & Vincent, 1998). (2) When the free water in the P(AA-co-AM) layer migrates to the middle layer, i.e. CTS coating, the water will penetrate the inner coating slowly in the initial stage and the dissolved NPK compound fertilizer in the core. In this stage, diffusion would be the release rate-limiting step. (3) Under the effect of water, ions and microorganisms existing in the soil, the middle CTS layer will slowly degrade in the last stage and continue to dissolve NPK compound fertilizer. In this stage, degradation rate determines the nutrients release rate. (4) The dissolved NPK compound fertilizer diffuses out the CTS layer and enters into the P(AA-co-AM) layer, and then releases into the soil through the dynamic exchange of free water.

The n value is an empirical parameter characterizing the release mechanism (Shaviv, 2000). On the basis of the diffusion exponent, an n value of 0.5 indicates the nutrient release mechanism approaches to a Fickian diffusion controlled release, whereas n equal to 1.0 indicates the nutrient release mechanism approaches to zero-order release. The n value from 0.5 to 1.0 is a nutrient release mechanism for non-Fickian diffusion or chain relaxation control release. From the plot of  $\log(M_r/M)$  versus  $\log(t)$  (Fig. 8), the release exponent (n) and release factor (K) have been calculated. Table 1 summarizes the values for N, P, and K

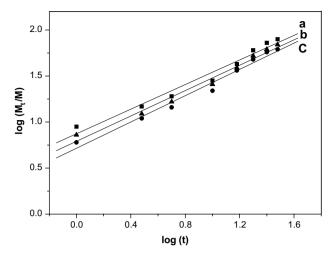


Fig. 8. Plot of release fractions of nutrient against time: nitrogen (a), potassium (b), and phosphorus (c).

Table 1 The release factors (K), release exponents (n), and determination coefficients  $(r^2)$  following linear regression of release data of nutrients from CFCW in soil

Nutrients	n	K	$r^2$
N	0.52	7.48	0.9851
K	0.54	6.19	0.9905
P	0.57	5.20	0.9899

release from CFCW in soil. The *n* value is in the range from 0.52 to 0.57. Therefore, the nutrients release mechanism is non-Fickian diffusion, and is controlled by a combination of diffusion of fertilizer from coating material and degradation rate of CTS layer. Additionally, due to the existing of many kinds of ions in soil solution, the swelling degree of P(AA-co-AM) is less in soil than that in distilled water, then the diffusion of soluble fertilizer in it would be difficult, which also contribute to slow release of nutrients from CFCW (Li & Wang, 2005).

## 3.5. The largest water-holding ratio of the soil

Besides its controlled-release property, another one of the most important characters of the CFCW we prepared is its water-retention capacity or, in other words, its effective utilization of water in arid and desert regions to transform them into "green and fertile lands". It was reported (Bakass, Mokhlisse, & Lallemant, 2002) that the use of superabsorbent polymer in the agricultural field could increase the largest water-holding capacity and water retention capacity of soil. Therefore, the experiments to test the water-holding capacity and water retention behaviors of soil with CFCW were performed. The experiment results of the largest water-holding ratio of the soil indicated that the largest water-holding ratio of the soil without CFCW was 30.17%, and that of the soil with CFCW was 40.35% (the mass ratio of CFCW to soil was 1:100), 10.18% higher

than the former. This showed that the CFCW we prepared still had excellent water absorbency in soil, could obviously improve the water-holding capacity of the soil, and could efficiently store rainwater or irrigation water resources. This was one of the significant advantages over the normal slow release fertilizers.

# 3.6. Water retention behavior of CFCW in soil

The most important application of CFCW is for agriculture and horticulture, especially for saving water in dry and desert regions and for accelerating plant growth. So, it is necessary to investigate the water-retention ability of CFCW in soil. Fig. 9 shows the water-retention behaviors of the soil with (a) and without (b) CFCW. From Fig. 9 we find that the addition of CFCW to soil could obviously increase the water-retention and decrease the water evaporation. The water retention ratio of soil without CFCW had only remained 12.4 and 2.6 wt% on the 10th and 20th days, respectively, while that of the soil with CFCW was 24.7 and 15.5 wt%, respectively. After 30 days, the soil without CFCW had already given off all the water, while the soil with CFCW still had 7.8 wt% water-retention ratios.

From this study, it could be inferred that CFCW had good water-retention capacity in soil, and that with CFCW use water can be saved and managed so that they can be effectively used for the growth of plant. These were the significant advantages over the normal slow release fertilizers, which always only had a controlled-release property. The reason was that the outer coating of CFCW could absorb and store a large quantity of the water in soil, and allow the water absorbed in it to be slowly released with the decrease of the soil moisture. Simultaneously, nutrition could also be released slowly with the water. Therefore, the swollen CFCW was just like an additional nutrient reservoir for the plant–soil sys-

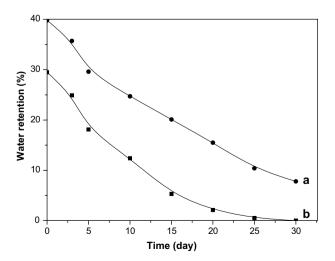


Fig. 9. Water retention behaviors of soil with CFCW (a) and soil without CFCW (b).

tem, and thus could increase the utilization efficiency of water and fertilizer at the same time. Furthermore, as we known, the chitosan in the first layer of the coating material was a biodegradable material (Borzacchiello et al., 2001) and the copolymer of AA and AM of the outer coating material can also be degradable in soil (Ye, Zhao, & Zhang, 2004), so the coating materials were not harmful to the soil. Thus there would be a good use potentiality in dry-prone regions.

### 3.7. Morphological analysis

From the SEM of the surface of the CFCW, it can be seen that the surface of CFCW is rugged, which structurally increased the surface area of the CFCW. Therefore, when CFCW is dipped in water, it can absorb water quickly to form a swollen hydrogel, which is responsible for the water-retention property of CFCW. The SEM of the cross-section of the CFCW shows the three-layers structure of CFCW. The outer layer is P(AA-co-AM) superabsorbent polymer, which could absorb a large amount of water. The middle layer is CTS, which serves as a physical barrier for mass transfer, and reduces the rate of water diffusion into the core and the nutrient diffusion outside the core, this provided the CFCW with a good controlled-release property. The inner core is a water-soluble NPK compound fertilizer granule. In summary, the outer P(AA-co-AM) layer enables the CFCW water-retention property, and the middle CTS layer enables the CFCW controlled-release property.

### 4. Conclusions

A chitosan-coated NPK compound fertilizer with controlled-release and water- retention (CFCW) was prepared, which possessed the three-layer structure. Its core was water-soluble NPK fertilizer granular, the inner coating was chitosan (CTS), and the outer coating was P(AA-co-AM) superabsorbent polymer. Element analysis and atomic absorption spectrophotometer results showed that the N, P and K contents were 8.06, 8.14 (shown by P<sub>2</sub>O<sub>5</sub>) and 7.98 (shown by K<sub>2</sub>O) wt%, respectively. The product had good slow release property, the nutrients released did not exceed 75% on the 30th day. The analysis of release showed that nutrient might be released from CFCW in soil by non-Fickian diffusion mechanism. The addition of CFCW into soil could greatly improve the water holding ability and water retention property of the soil. Moreover, this new approach showed promising in utilizing natural resource such as chitosan in the production of coating material, which could significantly reduce the production cost and make the technique quite environmental friendly. The results of the present work indicate that the CFCW was a good slow release fertilizer with excellent waterretention capability. Therefore, CFCW would find good application in agriculture and in the renewal of arid and desert environments.

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### References

- Abraham, J., & Rajasekharan, P. Y. N. (1996). Membrame-encapsulated controlled-release urea fertilizers based on acrylamide copolymers. *Journal of Applied Polymer Science*, 60, 2347–2351.
- Akelah, A. (1996). Novel utilizations of conventional agrochemicals by controlled release formulations. *Materials Science and Engineering*, C4, 83–98.
- Al-Zahrani, S. M. (1999). Controlled-release of fertilizers: Modeling and simulation. *International Journal of Engineering Science*, 37, 1299–1307.
- Bajpai, A. J., & Giri, A. (2003). Water sorption behaviour of highly swelling (carboxy methylcellulose-g-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical. *Carbohydrate Polymers*, 53, 271–279.
- Bakass, M., Mokhlisse, A., & Lallemant, M. (2002). 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. *Journal of Applied Polymer Science*, 83, 234–243.
- Borzacchiell, A., Ambrosio, L., Netti, P. A., Nicolais, L., Peniche, C., Gellardo, A., et al. (2001). Chitosan-based hydrogels: Synthesis and characterization. *Journal of Materials Science-Materials in Medicine*, 12, 861–864.
- Chen, Z. B., Liu, M. Z., & Ma, S. M. (2005). Synthesis and modification of salt-resistant superabsorbent polymers. *Reactive and Functional Poly*mers, 62, 85–92.
- David, S. G. H., & Mark, T. S. L. (1994). Water–polymer interactions and critical phenomena of swelling in inhomogeneous poly-(acrylonitrileacrylamide-acrylic acid) gel. *Polymer*, 35, 4416–4422.
- Flory, P. J. (1953). *Principles of polymer chemistry*. New York: Cornell University Press.
- Ge, J. J., Wu, R., Shi, X. H., Yu, H., Wang, M., & Li, W. J. (2002). Biodegradable polyurethane materials from bark and starch. II. Coating materials for controlled-release fertilizer. *Journal of Applied Polymer Science*, 86, 2948–2952.
- Guo, M. Y., Liu, M. Z., Zhan, F. L., & Wu, L. (2005). Preparation and properties of a slow-release membrane-encapsulated urea fertilizer

- with superabsorbent and moisture preservation. *Industrial and Engineering Chemistry Research*, 44, 4206-4211.
- Huacai, G., Wan, P., & Dengke, L. (2006). Graft copolymerization of chitosan with acrylic acid under microwave irradiation and its water absorbency. Carbohydrate Polymers, 66, 372–378.
- Jarosiewicz, A., & Tomaszewska, M. (2003). Controlled-release NPK fertilizer encapsulated by polymeric membranes. *Journal of Agricultural and Food Chemistry*, 51, 413–417.
- Kiatkamjornwong, S., & Wongwatthaasatien, R. (2004). Superabsorbent polymer of poly(acrylamide-co-acrylic acid) by foamed polymerization. I. Synthesis and water swelling properties. *Macromolecular Symposia*, 207, 229–240.
- Li, A., & Wang, A. Q. (2005). Synthesis and properties of clay-based superabsorbent composite. European Polymer Journal, 41, 1630–1637.
- Liang, R., & Liu, M. Z. (2006). Preparation and properties of a doublecoated slow-release and water-retention urea fertilizer. *Journal of Agricultural and Food Chemistry*, 54, 1392–1398.
- Lin, J., Wu, J., Yang, Z., & Pu, M. (2001). Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. *Macromolecular Rapid Communications*, 22, 422–424.
- Peng, X. H., Zhang, L. N., & Kennedy, J. F. (2006). Release behavior of microspheres from cross-linked N-methylated chitosan encapsulated ofloxacin. Carbohydrate Polymers, 65, 288–295.
- Qi, X. H., Liu, M. Z., Chen, Z. B., & Liang, R. (2007). Preparation and properties of diatomite composite superabsorbent. *Polymers for Advanced Technologies*, 18, 184–193.
- Shavit, V., Reiss, M., & Shaviv, A. (2002). Wetting mechanisms of gelbased controlled-release fertilizers. *Journal of Controlled Release*, 88, 71–83.
- Shaviv, A. (2000). Advances in controlled-release fertilizer. Advances in Agronomy, 71, 1–49.
- Smyth, G., Francis, X. Q., & Vincent, J. M. (1998). Water in hydrogels. 2. A study of water in poly(hydrooxyethl methacrylate). *Macromolecules*, 21, 3198–3204.
- Trenkel, M. E. (1997). International Fertilizer Industry Association. Stratospheric Ozone. HMSO. London.
- Ye, H., Zhao, J. Q., & Zhang, Y. H. (2004). Novel degradable superabsorbent materials of silicate/acrylis-based polymer hybrids. *Journal of Applied Polymer Science*, 91, 936–940.
- Zhang, J. P., Li, A., & Wang, A. Q. (2006). Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite. Carbohydrate Polymers, 65, 150–158.