

Multifunctional Slow-Release Organic–Inorganic Compound Fertilizer

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Multifunctional slow-release organic–inorganic compound fertilizer (MSOF) has been investigated to improve fertilizer use efficiency and reduce environmental pollution derived from fertilizer over-dosage. The special fertilizer is based on natural attapulgite (APT) clay used as a matrix, sodium alginate used as an inner coating and sodium alginate-*g*-poly(acrylic acid-*co*-acrylamide)/humic acid (SA-*g*-P(AA-*co*-AM)/HA) superabsorbent polymer used as an outer coating. The coated multi-element compound fertilizer granules were produced in a pan granulator, and the diameter of the prills was in the range of 2.5–3.5 mm. The structural and chemical characteristics of the product, as well as its efficiency in slowing the nutrients release, were examined. In addition, a mathematical model for nutrient release from the fertilizer was applied to calculate the diffusion coefficient *D* of nutrients in MSOF. The degradation of the SA-*g*-P(AA-*co*-AM)/HA coating was assessed by examining the weight loss with incubation time in soil. It is demonstrated that the product prepared by a simple route with good slow-release property may be expected to have wide potential applications in modern agriculture and horticulture.

KEYWORDS: Slow-release fertilizer; superabsorbent; attapulgite clay; humic acid

INTRODUCTION

Fertilizers are important indirect energy input for food production. Global fertilizer consumption increased by several orders of magnitude over the past 50 years (1). The data from 362 seasons of crop production indicated that at least 30–50% of crop yield is attributable to commercial fertilizers (2). However, most commercial fertilizers used in conventional agriculture are well-known for low efficiency of plant nutrient use, which leads to financial losses for farmers, poses a risk to the environment, and represents a waste of energy (3).

An effective way to mitigate this problem is to develop slow-release fertilizers (SRFs), which involve releasing nutrients in a slower manner than common fertilizers. SRFs play an important role in improving fertilizer use efficiency by reducing the frequency of application, thereby alleviating environmental pollution and leading to the development of sustainable agriculture (4). Coated fertilizers, physically prepared by coating fertilizer granules with various materials, are the major categories of the slow-release fertilizers (5–7). Moreover, hydrogel materials used as a matrix or coatings in SRFs have attracted more and more attention (8–10).

Hydrogels are defined as polymeric materials which exhibit the abilities of swelling in water and retaining a significant fraction of water within their structure. Taking into account the water imbibing characteristics of hydrogels, the possibility of their application in agricultural field has increasingly been investigated to alleviate certain agricultural problems, such as reducing irrigation water

consumption, improving nutrient retention in the soil, and increasing the soil's aeration (11–13).

Humic acid (HA) is a principal component of humic substances which are the major organic constituents of soil, peat, coal, dystrophic lakes and ocean water. It is produced by biodegradation of dead organic matter. It is a complex mixture of many different acids containing carboxyl and phenolate groups. As a kind of organic fertilizer, HA can regulate plant growth, accelerate root development, improve soil cluster and benefit the absorption of nutrient elements (14, 15). In this study, HA was introduced in superabsorbent polymer networks to fabricate a composite which was expected to improve the water-absorbing property and the degradation property and enhance nutritive functions of the superabsorbent materials for agricultural use.

Attapulgite (APT) is a crystalline hydrated magnesium silicate with one-dimensional nanostructures, large special surface area and moderate cation exchange capacity. In addition, it contains abundant elements, such as K, P, Ca, Mg, Si, Fe, and Mn (see **Table 1**). It is used in many traditional applications, and the major markets of this mineral are viscosity builders in drilling muds, environmental absorbents and agricultural carriers (16). APT resource is abundant in China, and the most abundant APT deposits are located in Anhui, Jiangsu and Gansu provinces. In order to broaden utilization of the natural resources, in this study, APT was used as an agricultural carrier and the source of many nutrient elements for plants. In addition, it is expected to make the fertilizer nutrients release slowly.

Our objectives in this work were to prepare a multifunctional organic–inorganic compound fertilizer that possesses attractive

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Table 1. Chemical Analysis of Natural Attapulgite

	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	K ₂ O	P ₂ O ₅	MnO
wt %	51.43	16.47	3.42	5.87	6.14	3.56	0.28	0.06

slow-release properties, and develop a kind of coating material capable of improving degradability, water-absorbing and water-holding properties. To accomplish these objectives, a double-coated fertilizer was prepared with APT as a matrix, sodium alginate as an inner coating and sodium alginate-g-poly(acrylic acid-co-acrylamide)/humic acid (SA-g-P(AA-co-AM)/HA) superabsorbent polymer as an outer coating.

MATERIALS AND METHODS

Materials. Sodium alginate (SA, the viscosity of 2% solution is 3200 mPa·s at 25 °C) was obtained from Qingdao Haiyang Chemical Co. (China). Acrylic acid (AA, chemical grade, Beijing Eastern Chemical Works, Beijing, China) was used as received. Acrylamide (AM) and humic acid (HA) were provided by Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. *N,N'*-methylene bisacrylamide (NNMBA) was recrystallized from 95% ethanol prior to use. Natural attapulgite (APT, supplied by Gansu Haozhou APT Co., China) was milled and sieved through a 200-mesh screen before use. All other chemicals were analytical grade and used as received.

Synthesis of SA-g-P(AA-co-AM)/HA Superabsorbents. A series of samples with different amounts of SA and HA were prepared according to the following procedure. A certain amount of SA was first dissolved in 20 mL of distilled water under vigorous stirring in a four-necked flask equipped with a stirrer, thermometer, and gas inlet tube. The solution was stirred and deaerated with nitrogen for 15 min. Then a solution of 2.67 g of AA (partially neutralized by an 8 mol/L NaOH solution), 1.33 g of AM, ammonium persulfate (APS), NNMBA, and HA was added to the flask dropwise and stirred constantly. The water bath was heated slowly to 75 °C and maintained at this temperature for 3 h. Finally, the resultant polymers were dried, milled, screened, and stored for further use.

Preparation of Multifunctional Slow-Release Organic–Inorganic Compound Fertilizer (MSOF). First, an amount of urea, KH₂PO₄, and APT powder (below 150 mesh) were mixed well. Then the mixture was placed on a rotating pan with urea granules (about 1.0–1.3 mm) in batches. The fertilizer cores were obtained under water atomization. Subsequently, SA powder (below 110 mesh) as the inner coating was adhered to the fertilizer cores by atomized CaCl₂ solution in the rotating pan. Finally, SA-g-P(AA-co-AM)/HA powder (below 110 mesh) as the outer coating was coated on the surface of the granules under rotating. The process was completed until a compact and homogeneous coating formed on the fertilizer granules. The coated granules were dried in an oven at 45 °C to obtain the final products.

Fourier Transform Infrared Spectroscopy Characterization. Fourier transform infrared (FTIR) spectroscopy of SA, HA, and SA-g-P(AA-co-AM)/HA was carried out with a KBr disk using a Nicolet NEXUS 670 FTIR spectrometer. In the case of SA-g-P(AA-co-AM)/HA, the dried products were extracted in a Soxhlet extractor with a solution of acetic acid and ethylene glycol (2: 3, v/v) for 72 h.

Component Analysis of MSOF. Content of nitrogen in the MSOF was determined with a 501 ammonia-selective electrode. The phosphorus and potassium contents in the MSOF were determined by an inductively coupled plasma (ICP) instrument (American TJA Corp., model IRISER/S).

Measurement of Water Absorbency of SA-g-P(AA-co-AM)/HA. The accurately weighed superabsorbents (0.2 g, 40–90 mesh) were 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

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

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

Effect of SA-g-P(AA-co-AM)/HA Superabsorbents on pH Value of Soil. Simulated soil solution samples with various pH values were

adjusted with 1 mol/L HCl or NaOH aqueous. 0.1 g of SA-g-P(AA-co-AM)/HA sample was immersed in 80 mL of soil solution with different pH values for 90 min. After the swollen hydrogels were filtered, the pH value of the filtrate was measured with a pH meter (pHS-3B, Shanghai Precision Scientific Instrument CO., Ltd., Shanghai, China).

Determination of Average Crushing Strength for MSOF. In the production of compound fertilizers, high quality refers to a free-flowing, hard, spherical and noncaking product. Fertilizer granules are required to have a mechanical hardness that will sufficiently withstand normal handling without fracture (17). In this study, average crushing strength was measured using compressing equipment for thirty granules (3 ± 0.5 mm in diameter), which was determined to be 26.5 N.

Slow Release Behavior of MSOF in Soil. Release rate of nitrogen (N), phosphorus (P₂O₅), and potassium (K₂O) from MSOF was determined by burying 1 g of MSOF in sealed plastic mesh bags approximately 5 to 6 cm below the surface of the soil in a plastic box at ambient temperature. Throughout the experiment, the soil moisture was kept at 20%. After 1, 3, 5, 10, 15, 20, 25, and 30 days, the mesh bags were retrieved and air-dried. Then the fertilizer granules were removed from the mesh bags and estimated for the nutrient content.

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

$$WH\% = \frac{(W_2 - W_1) \times 100}{200} \quad (2)$$

Degradation of SA-g-P(AA-co-AM)/HA Superabsorbents in Soil. Degradation of the superabsorbents was monitored by the dry weight loss. The SA-g-P(AA-co-AM)/HA superabsorbents with different amounts of SA and HA used in this experiment were prepared in a tube. They were cut into disks and then dried. The dried disks (9–10 mm in diameter and 0.5–0.6 mm in thickness) were buried 6 cm beneath the surface of the soil in a plastic box at ambient temperature. The soil moisture was kept at 20%. After 10, 20, 30, 50, 70, and 90 days, the disks were taken out, washed with distilled water and vacuum-dried to a constant weight. The percentage of degradation (PD %) of the superabsorbents was calculated from eq 3

$$PD\% = \frac{(W_0 - W_t)}{W_0} \times 100 \quad (3)$$

where W_0 and W_t are the weight of superabsorbent disks before and after degradation, respectively.

RESULTS AND DISCUSSION

Morphology and Characteristics of MSOF. Figure 1 shows the morphology of the MSOF samples. As shown in Figure 1, the samples are black round granules. The characteristics of MSOF are presented in Table 2.

FTIR Analysis of SA, HA and SA-g-P(AA-co-AM)/HA. The FTIR spectra of SA, HA and SA-g-P(AA-co-AM)/HA are shown in Figure 2. Some characteristic peaks in the SA spectrum (Figure 2a) can be ascribed as follows: 892 cm⁻¹ for the glycosidic bond stretching vibration, 1030 cm⁻¹ for C–O(H) stretching vibration, and 1615 and 1420 cm⁻¹ for the –COO⁻ asymmetric and symmetric stretching vibration, respectively. The characteristic peaks at 1705, 1594, 1246, and 1032 cm⁻¹ in the spectrum of HA (Figure 2b) could be assigned to the C=O stretching of the –COOH group, –COO⁻ asymmetric stretching vibration, phenolic C–O(H) stretching vibration and C–O(H) stretching vibration, respectively. For SA-g-P(AA-co-AM)/HA

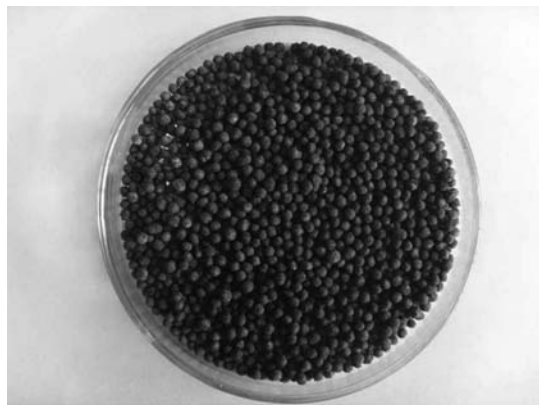


Figure 1. Morphology of the MSOF samples.

Table 2. Characteristics of MSOF

characteristics	value
nitrogen content	11.7%
phosphorus (P_2O_5) content	10.3%
potassium (K_2O) content	8.7%
APT content	35.5%
SA content	8.5%
SA-g-P(AA-co-AM)/HA content	15%
moisture content	2.1%
average crushing strength	26.5 N
diameter of dry sample	2.5–3.5 mm

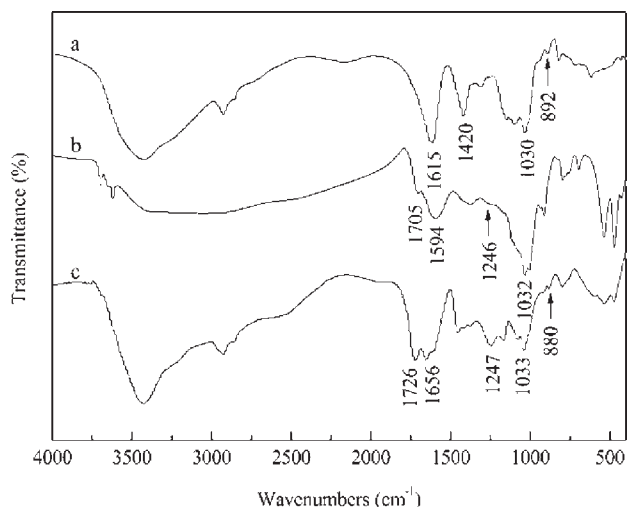


Figure 2. FTIR spectra of SA (a), HA (b) and SA-g-P(AA-co-AM)/HA (c).

(Figure 2c), it is noted that the characteristic peaks of PAA (1726 cm^{-1} for the C=O stretching of the $-\text{COOH}$ group) and PAM (1656 cm^{-1} for the C=O stretching of the $-\text{CONH}_2$ group) are observed. Meanwhile, there exist the characteristic peaks of SA (1033 cm^{-1} for the C–O(H) stretching, and 880 cm^{-1} for the glycosidic bonds), indicating the grafting reaction of AA and AM on SA. Moreover, only the band at 1247 cm^{-1} corresponding to the phenolic C–O(H) stretching vibration in HA could be used for positive identification of the introduction of HA, while the other characteristic bands of HA overlap with those of SA-g-P(AA-co-AM). Taken together, these results demonstrate that SA-g-P(AA-co-AM)/HA has been successfully prepared.

Effect of SA Content on Water Absorbency. One of the important properties of MSOF is the water absorbency due to the coating of

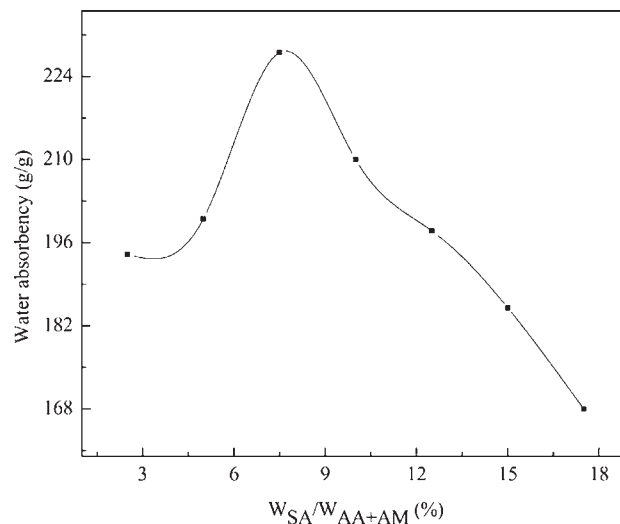


Figure 3. Effect of SA content on water absorbency.

SA-g-P(AA-co-AM)/HA superabsorbent polymers. To improve the water absorbency capacity of the products, the reaction parameters were optimized. The water absorbency as a function of SA content was investigated for SA-g-P(AA-co-AM)/HA superabsorbents, as shown in Figure 3. As we can see from Figure 3 (reaction conditions include the neutralization of AA, 60%; weight ratio of AA to AM, 2:1; HA, 10%; initiator, 1%; cross-linker, 0.06%; reaction time, 3 h; and reaction temperature, $75\text{ }^\circ\text{C}$), the maximum water absorbency is achieved when the SA content is 7.5 wt %. The water absorbency increases when the SA content is below 7.5 wt %, and decreases with higher content of SA. The reason for the change can be explained as follows: when the amount of SA content increases, more monomers would be grafted on the backbone of SA, which enhances hydrophilicity of corresponding superabsorbents and consequently causes an increase in water absorbency. When the amount of SA is larger than 7.5 wt %, the viscosity of the reaction mixture increases, which hinders the movement of the reactants (18). Thus, the grafting ratio and the molecular weight of the grafted PAA chains decrease, resulting in a decrease in water absorbency.

Effect of HA Content on Water Absorbency. The effect of the amount of HA in the superabsorbent composite on the water absorbency is shown in Figure 4. It is found that when a suitable amount of HA is incorporated, the swelling capacity of the SA-g-P(AA-co-AM)/HA superabsorbents significantly improves. The maximum water absorbency reaches 228 g/g in tap water when the HA content is 10 wt %. HA contains a large number of hydrophilic groups, such as carboxyl, hydroxyl, and amido, which could react with SA-g-P(AA-co-AM) during the polymerization process and then the hydrophilicity of the polymeric network is improved. However, when the content of HA in the superabsorbent composite is larger than 10 wt %, the water absorbency decreases with further increase in the amount of HA. This may be attributed to the fact that a further increase in the HA content may result in the cross-linking degree increasing and the same for the number of elastically chains. Meanwhile, excessive HA only acts as a filler of the composite and reduces the water absorbency (19, 20).

Effect of SA-g-P(AA-co-AM)/HA Superabsorbents on pH Value of Soil. Soil pH affects all chemical, physical, and biological soil properties (21). Soil carries nutrients such as nitrogen (N), phosphorus (P), and potassium (K) that plants need in specific amounts to grow, thrive, and fight off diseases. Previous studies showed that soil nutrients are most available to plant roots when soil pH is in

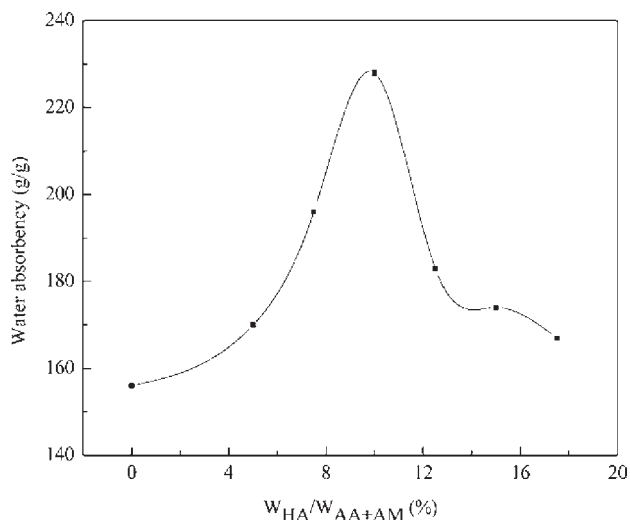


Figure 4. Effect of HA content on water absorbency.

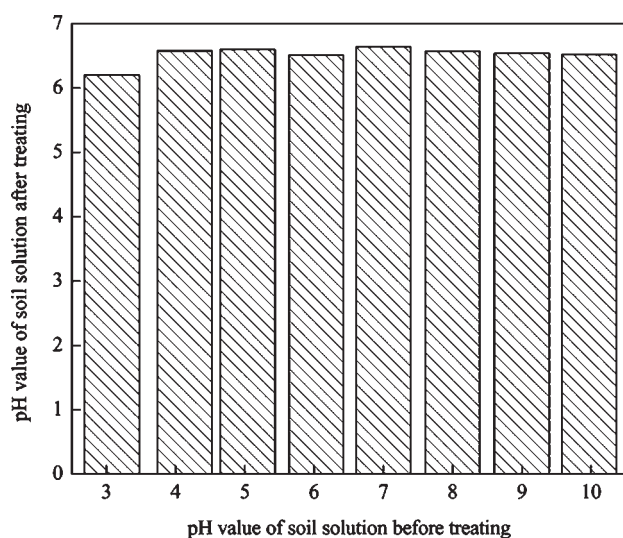


Figure 5. Effect of SA-g-P(AA-co-AM)/HA superabsorbents on pH value of soil.

the range of 5.5–7.0 and plants may show symptoms of nutrient deficiency or toxicity at very low or high soil pH (22). Soil pH also affects soil microbial biomass and microbial activity. The microbial biomass is not only the catalyst of all microbial transformations in soil, but also constitutes a pool of nutrients that has a rapid turnover compared with soil organic matter (23). It was reported that microbial biomass and microbial activity tend to stabilize at pH values between about 5 and 7 (22). In this study, the effect of SA-g-P(AA-co-AM)/HA superabsorbents on pH value of soil is investigated and shown in Figure 5. As we can see from Figure 5, the various pH values of the simulated soil solution are adjusted to about 6.5 after treating with the superabsorbents. This is because SA-g-P(AA-co-AM)/HA superabsorbents contain large amounts of $-\text{COOH}$ and $-\text{COO}^-$ groups. $-\text{COOH}$ groups can react with OH^- of the soil solution under a basic condition, and $-\text{COO}^-$ groups can react with H^+ of the soil solution under an acidic condition. In other words, the pH value of the soil solution was balanced with the buffer action of the superabsorbents (24). Therefore, SA-g-P(AA-co-AM)/HA superabsorbents used in this study not only absorb water to enhance plants survival in arid environment but also adjust pH value of soil as a kind of soil amendment, which may provide a solution to problems associated with acid or basic soil.

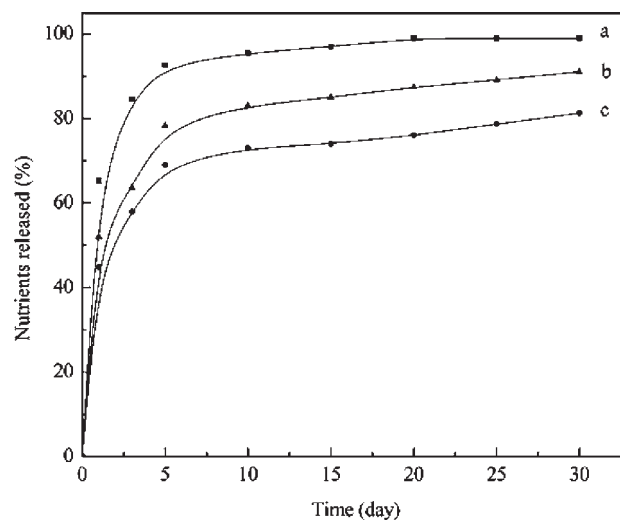


Figure 6. Slow-release behavior of nitrogen (N) (a), potassium (K_2O) (b), and phosphorus (P_2O_5) (c) from MSOF in soil.

Slow-Release Behavior of MSOF in Soil. Figure 6 shows the slow-release behavior of nitrogen (N), phosphorus (P_2O_5), and potassium (K_2O) from MSOF in soil at room temperature. As shown in the figure, the release rate of nitrogen is higher than that of phosphorus and potassium, almost released completely during 30 days. This is because the solubility of urea is great and, as a neutral organic molecule, urea cannot be adsorbed easily by the charged SA-g-P(AA-co-AM)/HA superabsorbents and APT. Therefore, it would quickly dissolve in the soil solution after being immersed in soil. However, compared with the untreated urea granules, of which 98.5 wt % of N was released within 12 h (25), the slow-release property of nitrogen in MSOF is improved to some extent. The nutrients phosphorus and potassium have a lower release rate than nitrogen, 81.3 wt % and 91.1 wt % within 30 days, respectively. The rapid release in the early stage (in 5 days) can be mainly ascribed to the dissolution of KH_2PO_4 which was filled physically in the fertilizer cores. The release rate after 5 days is low. This is mainly due to the physical barrier of the inner coating SA and outer coating superabsorbents. Meanwhile, the high adsorption capacity of APT also makes the nutrients release slowly. As mentioned before, APT has high special surface area and there are many parallel channels through the lattice. When water diffuses into fertilizer cores, part of the nutrients would be adsorbed by APT, which consequently slows the release rate of nutrients.

To gain more insight into the release property of MSOF, the release data of MSOF in soil was analyzed by applying the mathematical model proposed by Al-Zahrani (26):

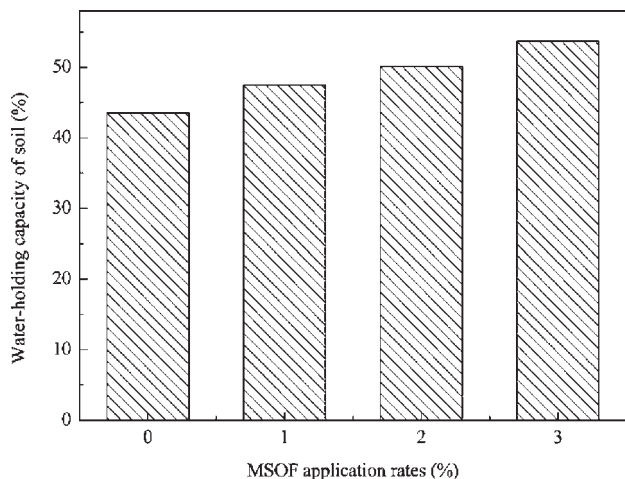
$$\frac{M_t}{M_0} = 6(1 + \alpha) \left(\frac{tD}{\pi R^2} \right)^{0.5}$$

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

where M_t/M_0 is the fractional nutrient release at time t ; D is the diffusion coefficient; R is radius of the fertilizer granule; C_0 is initial concentration of the fertilizer; and C_∞ is the concentration of the fertilizer in the sphere at infinite time. The data of the slow-release experiment show that the nutrients nitrogen, phosphorus, and potassium released over 99% during 60 days (data not shown). Therefore, C_∞ is supposed to be zero in this study. Table 3 shows the values of D for nitrogen (N), phosphorus (P_2O_5), and potassium (K_2O) released from MSOF in soil. The value of D for N is greater

Table 3. Diffusion Coefficient (*D*) for N, P, and K Released from MSOF in Soil

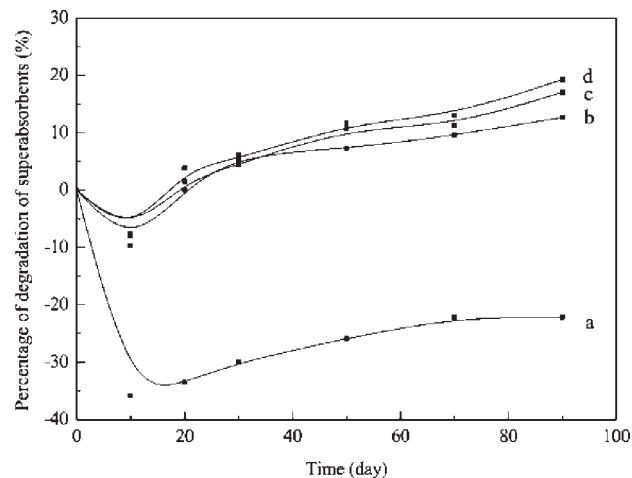
	N	P	K
<i>D</i> (mm ² /day)	0.55	0.38	0.49

**Figure 7.** Water-holding capacity of soil with different MSOF application rates.

than the values for P₂O₅ and K₂O, indicating that the release rate of N is higher than that of P₂O₅ and K₂O, which is in agreement with the slow-release behavior of nutrients in MSOF. From the results, we think that the MSOF could improve the utilization of fertilizer nutrients efficiently and then alleviate the environmental pollution resulted from fertilizer overdosage.

Water-Holding Capacity of Soil with MSOF. The presence of water in soil is essential to vegetation. Liquid water ensures the feeding of plants with nutritive elements, which make it possible to obtain a better growth of plants. Taking into account the interesting particular characteristics of the water absorption capacity of the MSOF, we studied its effect on water-holding capacity of soil, as shown in **Figure 7**. The water-holding capacity of soil is 43.5, 47.5, 50.1, and 53.7% for MSOF application rate of 0, 1, 2, and 3%, respectively. It is noted that, with the increase of MSOF samples, the superabsorbent contents increase and thus the water-holding capacity of the soil increases. However, comparison of the water retained by the superabsorbents in tap water (**Figures 3 and 4**) with those in soil shows a significant difference. The superabsorbents in soil retain much less water. In soil, each MSOF granule is surrounded by soil particles and subjected to a confining pressure by these particles (27). Therefore, the swelling degree of the superabsorbents in soil is limited compared with that in tap water. However, compared with the control (soil without MSOF), the MSOF effectively improves the water-holding capacity of soil, even though at low application rate. Consequently, the use of MSOF in the agricultural field could reduce water losses by evaporation and infiltration.

Degradation of Superabsorbents. Recently, as the primary product of superabsorbents, the polyacrylate cannot be widely used because of its poor degradability in soil and its accumulation over time to become a new type of pollution (28). In this work, SA and HA were introduced in the network to improve the degradability of the superabsorbents. The degradation process was evaluated by a simple method of weight loss, which has been employed widely by other researchers (29–31). **Figure 8** depicts the weight loss of superabsorbents with different amounts of SA and HA with incubation time in soil at ambient temperature. As shown in **Figure 8**, a decrease in weight with time demonstrates the degradability of the hydrogels and the percentage of degradation

**Figure 8.** Degradation of superabsorbents with different amounts of SA and HA: (sample a) 0% SA and 0% HA; (sample b) 7.5% SA and 0% HA; (sample c) 15% SA and 0% HA; (sample d) 7.5% SA and 10% HA.

(PD %) increases with increasing SA and HA contents. During the period investigated, the sample with 7.5% SA and 10% HA loses weight faster than the others whereas the sample with 0% SA and 0% HA shows no weight loss. After 90 days, the final PD values are -21.7, 12.7, 17.1, and 19.3% for samples a, b, c, and d, respectively. Sample a exhibits a negative PD value, indicating that it is not degraded within 90 days. It is understandable that, with increasing the amount of SA and HA in the composite, a greater number of SA and HA molecules encounter approaching soil micro-organism, and hence the PD values increase. For instance, for the sample d with 7.5% SA and 10% HA, the swelling ability of the sample is greatest, and the pore size of the superabsorbents has already widened due to this enhanced swelling; then more soil micro-organism is imbibed by the swollen superabsorbents. Obviously, the soil microorganism invades the surface and network of the hydrogels and results in an increased PD value.

During the initial stage of degradation (in 10 days), the degradation of a small number of SA or HA cannot damage the whole hydrogel network, but the lattice size of the network will enlarge. As a result, the swelling ratio of the superabsorbents increases, and more ions and soil particles are absorbed by the superabsorbents. This may explain why there is a weight increase in the first 10 days for all cases.

It is worth noting that the SA-g-P(AA-co-AM)/HA superabsorbent materials are partially degradable and can be applied in agriculture as a new kind of coating materials to alleviate environmental pollution.

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Received for review July 28, 2010. Revised manuscript received October 25, 2010. Accepted October 26, 2010. We gratefully acknowledge the financial support of the Special Doctorial Program Funds of the Ministry of Education of China (Grant No. 20090211110004) and Gansu Province Project of Science and Technologies (Grant No. 0804WCGA130).