Salt-Tolerant Superabsorbent Polymer with High Capacity of Water-Nutrient Retention Derived from Sulfamic Acid-Modified Starch

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ABSTRACT: The application of superabsorbent polymers (SAPs) is hindered because their absorption capability is greatly affected by the electrolytes in a solution. A novel modified water-absorbent polymer was fabricated by solution polymerization of sulfamic acid-modified starch and acrylic acid; the swelling ratios of this absorbent polymer were 1026 g/g in deionized water and 145 g/g in 0.9% sodium chloride solution and increased by 99.5 and 13.4%, respectively, when compared with ordinary starch-grafted acrylic SAPs. The water absorption capacity was measured in water at different pH values, salt concentrations, and temperatures. In addition, water and fertilizer retentions were studied by simulated leaching tests in a soil column. The results showed that water absorption capacities of the modified SAP in salt solutions were improved due to the adsorption and transfer of water molecules by the sulfonic acid groups. Compared to the losses when there was no superabsorbent treatment, the water, nitrate, ammonium nitrogen, and water-soluble potassium losses during the salt-tolerant superabsorbent treatment were significantly reduced by 18.5, 22.8, 88.0, and 63.8%, respectively. The method introduced in this study could guide the development and wide application of salt-tolerant SAPs in agriculture and horticulture.

1. INTRODUCTION

Superabsorbent polymers (SAPs) typically consist of cross-linked linear (or branched) hydrophilic polymers with three-dimensional networks that can absorb large quantities of water or biological fluids, and because of this characteristic, SAPs have been widely used in medical and health applications, sewage treatment, and water conservation. When SAPs are applied to soil, the soil surface water evaporation and water infiltration could be reduced, and soil porosity and soil structural stability could be improved; SAPs could also reduce soil bulk density, improve water use efficiency, and improve soil synchrony and carbon assimilation rate in the early stage of plant growth. SAPs could also improve the utilization efficiency of granular fertilizer, so that the absorbent polymers are also widely used in agriculture and forestry. Typically, water-absorbing polymers undergo swelling in three stages. First, the surface of the polymer is wetted by contact with water molecules, which are combined with the hydrophilic groups on the surface. Second, the water molecules enter the micropores in the polymer molecules, which results in an increase in the molecular volume of the polymer. In the third stage, the binding force of the molecular skeleton and the osmotic pressure of water reach an equilibrium state, and the maximum water absorption capacity and volume of the polymer is achieved. However, the hydrophilic groups inside the polymer bind salt ions easily by a mechanism similar to complexation. Therefore, the network structures are blocked, hindering the entry of water molecules in the first and second stages and volume expansion of the polymer in the third stage. Consequently, the water absorption capacity decreases sharply in water-containing electrolytes, such as urine, blood, or soil solutions. Furthermore, these polymers are not easily degraded and might cause harm to humans and the environment because they are often made from petrochemical materials. To solve these problems, previous researchers found that increasing the number and type of hydrophilic groups could improve the salt tolerance. Natural organic polymer materials that have hydrophilic groups, such as starch, fiber, chitosan derivatives, and minerals (clay, montmorillonite, etc.) could be used to improve the degradability and salt tolerance of these materials. Starch, a natural bioresource formed by the polymerization of glucose molecules, is among the most widely used polysaccharides in SAP production. However, most starch-based SAPs still suffer from poor water absorption and low salt tolerance. Peng et al. prepared SAPs from sodium-starch...
sulfonate and acrylic acid and improved the SR in deionized water. However, sodium-starch sulfonate was prepared by synthesizing a complex intermediate via a 2-step method. When the starch was treated by the highly polar intermediate complex, its structure could be destroyed. The water absorption of the final product was only 91 g/g in physiological saline, demonstrating its low salt tolerance. Furthermore, solvents used in the synthesis, such as acetone, could cause harm to humans and the environment. Acid-treated starch is prepared by treating starch or starch granules with inorganic acids, which break the long chains into short chains without changing the structure. Sulfamic acid is a moderately strong acid and might be considered to be an intermediate compound between sulfuric acid and sulfamide. It has desirable water descaling properties, low volatility, and low toxicity compared to most common strong mineral acids. Moreover, when sulfamic acid is used as a modifier to treat starch, the number of strongly hydrophilic sulfonic acid groups can be increased to obtain acid-modified starch. It is hypothesized that using acid-modified starch might improve the hydrophilicity and salt tolerance of starch-based SAPs. Based on the literature, acid-modified starch is commonly used in food science; however, none of these studies attempted SAP synthesis.

To reduce the effects of salts on SAPs by exploiting the unique groups and structures of acid-modified starches, a simple novel method for preparing a water-absorbing polymer by an aqueous polymerization process was developed. The number of sulfonic acid groups was higher in the acid-denatured starch, thereby providing the SAPs with salt tolerance and a high water absorption capacity and expanding their application range.

2. RESULTS AND DISCUSSION

2.1. Swelling Kinetics and Effects of the Simulated Application Conditions on the SR of the Salt-Tolerant Superabsorbent Polymer. To determine the mechanism and rate of salt-tolerant superabsorbent polymer (STSP) swelling in deionized water, a swelling kinetic study was performed by applying pseudo-first-order and pseudo-second-order kinetic models. The SR was calculated based on the mass after complete swelling divided by the dry mass. Symbols with error bars represent treatment means ± SEs based on a one-way ANOVA (P > 0.05).

Table 1. Summary of the Best-Fit SR Convergence Values (SR_c) and Rate Constants (k) of 2 Swelling Kinetic Models for CSAP, SGSP, and STSP

| model       | parameter 1     | parameter 2     | R^2  |
|-------------|-----------------|-----------------|------|
| CSAP        | pseudo-first-order | SR_c = 269.26  | k_1 = 0.045  | 0.9620 |
|             | pseudo-second-order | SR_c = 277.78  | k_2 = 4.5 \times 10^{-4} | 0.9679 |
| SGSP        | pseudo-first-order | SR_c = 469.26  | k_1 = 0.018  | 0.9859 |
|             | pseudo-second-order | SR_c = 502.51  | k_2 = 7.8 \times 10^{-5} | 0.9861 |
| STSP        | pseudo-first-order | SR_c = 1076.27 | k_1 = 0.023  | 0.9749 |
|             | pseudo-second-order | SR_c = 1240.84 | k_2 = 2.0 \times 10^{-5} | 0.9256 |

Figure 1. SRs of a CSAP, SGSP, and STSP in deionized water as a function of time (a), pH (b), salt concentration (c), and temperature (d). The SR (g/g) was calculated based on the mass after complete swelling divided by the dry mass. Symbols with error bars represent treatment means ± SEs based on a one-way ANOVA (P > 0.05).
Moreover, the SR of the STSP was significantly higher than that of the CSAP in deionized water at different pH values and salt contents, and the highest values were 1020 and 514 g/g, respectively, at pH 7–8 (Figure 1b). The SRs of the three SPs decreased with increasing salt concentration (Figure 1c). Moreover, the SR of the STSP was significantly affected by the pH. Temperature had the smallest effect on the SR of the SGSP in deionized water, and the SR of the STSP decreased significantly when the temperature was higher than 45 °C (Figure 1d). This result was probably due to temperature effects on the diffusion coefficient of water. At higher temperatures, the molecular motion increased. Because the molecular skeleton of the STSP was acid-treated to obtain short-chain starch,22 it was less stable than the starch skeleton of the SGSP and the polyolefin skeleton of the CSAP at higher temperatures. However, this short-chain skeleton might improve the degradation ability of the STSP and would decrease environmental pollution. It is rare to reach high temperatures above 45 °C under the conditions of real natural soil applications. Therefore, within a reasonable range, the STSP still exhibited a higher performance than the SGSP and CSAP.

2.2. Structure and Characterization of the SGSP and STSP. The FTIR spectroscopy results showed that the STSP (Figure 2a), SGSP (Figure 2b), acid-modified starch (Figure 2c), and starch (Figure 2d), all had strong, broad absorption peaks at 3300–3500 cm⁻¹ and a weak absorption peak at 1600–1650 cm⁻¹ (Figure 2), which corresponds to the vibrational and scissoring vibration absorption characteristics of −OH30 and is the main characteristic absorption peak of starch. The STSP and acid-modified starch exhibited obvious absorption peaks at 1205 and 800 cm⁻¹ (Figure 2a,c), which are the characteristic symmetric vibrations of −SO₃H33 and characteristic vibrations of C−S,32 respectively. The STSP also had a vibrational absorption peak attributed to C=O30 at 1720 cm⁻¹ and an asymmetric vibration absorption peak corresponding to SO₃H at 1400 cm⁻¹ (Figure 2a). The acid-modified starch had a symmetric vibration absorption peak due to SO₃H at 1180 cm⁻¹ (Figure 2c), and these absorption peaks were not observed in the SGSP and starch spectra (Figure 2b,d), which indicates that the sulfonic acid group was added to the starch molecule by the modification treatment and was retained in the STSP. These results were consistent with the energy-dispersive X-ray spectra (Figure 3a,b); the amounts of sulfur and oxygen in the STSP sample were higher.

The microstructures of the SGSP and STSP in the equilibrium swelling state in deionized water were almost the same, but the surface of the STSP was smoother and denser. The equilibrium swelling states in physiological saline were significantly different. The microscopic pores of the SGSP were almost completely filled with salt. These salt crystals hindered the entry of water molecules and the expansion of the SGSP molecules, thereby reducing the water absorption capacity. The microscopic network structure of the STSP was largely retained, and salt crystals covered only a small part of the surface. This result was due to the introduction of various hydrophilic groups (especially sulfonic acid groups). When the STSP swelled in a salt solution, the water molecules were first
adsorbed by the sulfonic acid groups and transferred to adjacent sulfonic acid groups,\textsuperscript{33,34} which led to a much higher water transport rate compared to the salt diffusion rate. Inside the equilibrium swollen STSP, the salt content was much lower than in the external solution. Thus, at the microscopic level, the salt crystallization inside the STSP was much less than that inside the SGSP (Figure 4).

\textbf{Figure 4.} Scanning electron microscopy (SEM) images of (a) SGSP in deionized water, (b) STSP in deionized water, (c) SGSP in saline water, and (d) STSP in saline water.

\section*{2.3. Effects of the Synthesis Conditions on the STSP SR.} In an acid environment, the starch became a short-chain molecule, and the number of hydrophilic groups increased. The amounts of the modifiers affected the formation of the small molecules, and the water absorption ability of the final polymer was also affected. With increasing modifier dosage, the water absorption capacity first increased and then decreased, and the absorption capacity in normal saline also increased significantly. When the mass dosage of the modifier was 1.2\% of the starch mass, the maximum water absorption capacity was achieved (Figure 5a).

Acrylic acid was grafted onto the starch to serve as a binding site for the backbone. The proportion of modified starch and acrylic acid also affected the water absorption capacity of the polymer.\textsuperscript{27} When the proportion of starch was higher, the number of intermolecular bonding points decreased, and the polymer pores were enlarged. Accordingly, the contact density of the hydrophilic groups with water was reduced, leading to a decrease in the SR. When the ratio of starch was too low, the molecular skeleton was tightly bound, and the swelling was limited. The optimal mass ratio of modified starch to acrylic acid was 1:7:5 (Figure 5b).

Acrylic acid was partially neutralized to form sodium acrylate. During polymerization in the aqueous solution, sodium propanoate was present in the dissociated carboxylate salt form.\textsuperscript{35} At a higher degree of dissociation, the molecular chain was extended moderately, and the formation of the polymerization network was favorable. The results indicated that at 70\% neutralization, the absorption function was at a maximum (Figure 5c). According to Flory’s polymer swelling theory,\textsuperscript{36} as the degree of crosslinking increased, the swelling capacity decreased. The SR was also affected by the initiator and the crosslinking agent. The maximum water absorbency was achieved with 3\% ammonium persulfate (APS) and 0.15\% MBA [percent of acrylic acid (AA) mass] (Figure 5d,e).

\section*{2.4. Effects of the STSP on Water and Fertilizer Leaching in Soil Columns.} The water absorption capacities of the three SAPs were directly reflected by the total volume of the leachate. Without fertilizer in the CKSAP (control check adding superabsorbent polymers) treatment, the maximal water absorption capacity of the STSP and smallest leachate volume were observed (Figure 6a). The CKF (control check adding fertilizer) treatment, which did not include a SAP, could be considered to give the water retention capacity of the soil itself. Compared to the CKF treatment, the water loss was decreased by 11.1, 12.5, and 18.5\% with the CSAP, SGSP, and STSP treatments, respectively, which demonstrated that all three SAPs effectively reduced water loss (Figure 6a).

Nitrogen is one of the most important nutrient elements in agricultural production.\textsuperscript{37} Soil fertility can be directly reflected by the nitrate and ammonium nitrogen concentrations in the soil. Nevertheless, nitrogen is easily leached. The CKSAP treatment with STSP application but no fertilizer resulted in very little leaching (Figure 6b). The CKF treatment could be considered to show the leaching loss under normal conditions. The leaching losses of nitrate nitrogen for the SGSP and STSP treatments were significantly reduced by 22.3 and 22.8\%, respectively, compared to that of the CKF treatment, but the difference between the CSAP and CKF treatment results was not significant (Figure 6b). The ammonium nitrogen leaching losses for the CSAP, SGSP, and STSP treatments were significantly reduced by 51.6, 72.4, and 88.0\%, respectively, compared to that for CKF (Figure 6c), probably because the soil was negatively charged and the internal hydrophilic groups of SAPs were also anionic.\textsuperscript{38} Inside the SAP, the cation (K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, and so on) was combined with the hydrophilic group by a method which was similar with complexation,\textsuperscript{39} but with weak ionic bonds, no coordinate bond was formed and because the larger the hydration radius, greater is the positive charge, which came to the stronger of the generated ionic bonds.\textsuperscript{40}

When the ion concentration outside the SAPs was low, the bound cation could also diffuse outward, thus causing the absorption and release characteristics of nutrients.

Potassium is also an important nutrient element in agricultural production. The potassium leaching losses for the CSAP, SGSP, and STSP were significantly reduced by 57.3, 18.8, and 63.8\%, respectively, compared to that for CKF (Figure 6d). It should be noted that the potassium ion leaching was higher with the SGSP than with the CSAP and STSP, which might be due to the large amount of sodium ions between the SGSP and STSP molecules (Figure 3a,b). The sodium ions and potassium ions from the soil and fertilizer competed in the processes of adsorption and migration.\textsuperscript{41}

Because the SGSP had fewer hydrophilic groups than the STSP, the binding of the sodium ions was weaker in the SGSP than in the STSP. The sodium ions in the SGSP were partially eluted and replaced the potassium ions at the adsorption sites in the soil, which led directly to higher potassium ion leaching during the SGSP treatment than during the STSP treatment.

\section*{3. CONCLUSIONS}

A biobased SAP was successfully synthesized from acid-denatured starch and acrylic acid. The prepared copolymer had a different structure and swelling characteristics than ordinary starch-grafted acrylic acid, and it exhibited excellent water absorption and salt tolerance with SRs of 1026 g/g in deionized water and 155 g/g in a 0.9\% sodium chloride solution. Water, nitrate, ammonium nitrogen and water-soluble
potassium losses were significantly reduced by 18.5, 22.8, 88.0, and 63.8%, respectively, when the STSP treatment was applied instead of the CKF treatment in simulated soil column tests. This novel polymer has great potential for large-scale commercial applications and might have broad applications in agriculture and forestry.

4. MATERIALS AND METHODS

4.1. Materials. Soluble starch and APS (analytical grade) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). AA (chemically pure), amino sulfonic acid (ASA, analytical grade), and MBA (chemically pure) were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and Moisture Plus Watering Crystals (Schultz, Wisconsin, America), which are white translucent solid particles with SR of 1026 g/g in deionized water and 155 g/g in 0.9% sodium chloride solution, were employed as the CSAP.

4.2. Syntheses of the STSP and SGSP. Soluble starch was dissolved in deionized water to a mass concentration at 40% and homogenized in a glass beaker. The mixture was heated at 50 °C in a water bath with mechanical agitation for 2 h. The starch homogenate was poured into flat plates, oven-dried at 50 °C for 2 h, and then ground to a powder. Then, the starch homogenate powder was mixed with water in a powder: water mass ratio of 0.4:1 in a three-neck flask. The initiator ammonium persulfate was added to the starch homogenate mixture. The resulting solution was stirred and heated at 50 °C. Acrylic acid, which was 6–12 times the weight of the added starch, was neutralized with a 5 mol/L sodium hydroxide solution at 0 °C and then added to the starch homogenate mixture. MBA was added as a crosslinker, and the reaction was performed in a water bath at 50 °C for 1 h. Nitrogen gas was inserted for protective purpose during the entire reaction process. After 2 h, the thick colloidal crude product mixture was washed with deionized water to remove the unreacted monomer. It was then dried at 50 °C in a blast dryer (60–72 h) and crushed by a stainless steel pulverizer with 10–20 mesh sieves.

To prepare the SGSP, soluble starch was used as the raw material, and it was not treated with ASA. The rest of the synthesis steps were exactly the same as those for the STSP.

4.3. Measurements of Swelling Capacity of the SGSP, STSP, and CSAP. The SR was measured using the tea bag method in which a certain mass (M1) of the dry material was fully soaked in deionized water. After complete expansion, it was removed and held until water was no longer dripping from the bag. The weight of the soaked STSP (M2) was recorded.
and the SR was calculated using the following formula: $SR = (M_2 - M_1)/M_1$, where $M_1$ and $M_2$ are the weights of the dry and swollen samples (g), respectively. The expansion kinetic equation fitting was performed by measuring the SR at 10, 20, 30, 40, 50, 60, 90, 120, 150, 210, 390, and 600 min after soaking. The SRs of the three SAPs (CSAP, SGSP, and STSP) were measured at pH values of 3, 4, 5, 6, 7, 8, 9, and 10; sodium ion concentrations of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0%; and temperatures of 5, 15, 25, 35, 45, 55, and 65 °C.

4.4. Characterization of the STSP and SGSP. FTIR spectra were obtained on a Nicolet 6700 FTIR spectrometer (Nicolet, Waltham, America). The SEM images and energy spectra were obtained on a Tecnai G2-F20 transmission electron microscope (EFIS-TWIN, Hillsboro, America) using freeze-dried samples.

4.5. Measurement of Water and Nutrient Retention. The soil for these experiments was sampled from Taian, Shandong, China (117°9′48″E, 36°9′40″N) and was classified as a Typic Hapludalf.2 The basic physicochemical properties of the soil are: organic matter, 11.7 g/kg; NH$_4^+$-N, 13.8 mg/kg; NO$_3^-$-N, 28.2 mg/kg; Olsen-P, 65.6 mg/kg; and water-soluble potassium, 168 mg/kg. The soil was air-dried and passed through a 2 mm sieve. A compound fertilizer ($N$−$P_2O_5$−$K_2O$ 1−8−11, BASF, Germany) was used.

Single factor design was used in this experiment. CKSAP indicated no fertilizer; CKF indicated no SAP (control treatment); and CSAP, SGSP, and STSP indicated the separate treatments with one of the three SAPs (CSAP, SGSP, and STSP, respectively) and the same amount of fertilizer.

The columns were constructed from polyvinyl chloride (PVC) tubes, each with a diameter of 7.5 cm and length of 60 cm. Then, nylon mesh was fixed at the bottom of each PVC tube. First, 1 kg soil was packed into the bottom of the soil column and compacted. Then, 1 kg soil completely mixed with 6.00 g fertilizer and 3.75 g SAP was loaded into the soil column. The soil bulk density was 1.299 g/cm$^3$, and the soil volume was 1540 cm$^3$. Finally, irrigation was performed four times. The water volume of each irrigation was 100% of the soil pore volume, and the leaching solution was collected until no liquid continued to flow out of the soil column. The leachate volume and NO$_3^-$−N, NH$_4^+$−N, and water-soluble potassium contents were determined by flow analyzer (AA-3, SEAL, Germany) and flame photometer (M410 Sherwood, United Kingdom).

4.6. Data Analyses. All experiments and analytical measurements were conducted in triplicate. The mean values are shown in the plotted data with the standard deviation represented by error bars. A paired sample $t$-test analysis was conducted using SAS 8.1 to evaluate whether the differences between the means were significant ($P < 0.05$).

To evaluate and compare the swelling characteristics of the materials, pseudo-first-order and pseudo-second-order26 equations were used to simulate the experimental kinetic data

$$SR_{t} = SR_C(1 - e^{-k_1t}), \quad \text{pseudo - first - order}$$

$$SR_{t} = \frac{k_2SR_C^2}{1 + k_3SR_Ct}, \quad \text{pseudo - second - order}$$

where $SR_t$ (g/g) and $SR_C$ (g/g) are the cumulative ratios of swelling at time, $t$ and at equilibrium, respectively, and $k_1$ (min$^{-1}$) and $k_2$ (g/(g-min)) are the first- and second-order swelling rate constants, respectively.

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Figure 6. Total leaching water volume (a) and NO$_3^-$ (b), NH$_4^+$ (c), and water-soluble potassium (d) leaching losses from different fertilizers during SAP treatments. Bar heights represent means and error bars represent ±SE. Within each graph, means followed with the same letter were not significantly different based on a one-way ANOVA followed by Duncan’s multiple-range tests ($P > 0.05$).
ACKNOWLEDGMENTS

This study was supported by the National Key Research and Development Program of China (Grant no. 2017YFD0200706) and the National Natural Science Foundation of China (Grant no. 41571236).

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