

Preparation of an Attapulgite-Modified Composite Hydrogel and Application in an Environmentally Responsive Green Fertilizer

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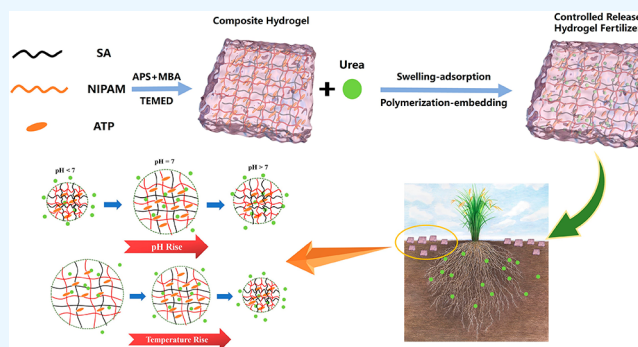
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ABSTRACT: Conventional fertilizers suffer from uncontrollable nutrient release rates and low utilization efficiency, which lead to environmental issues. An environmentally responsive fertilizer that can regulate nutrient release in response to environmental fluctuation is considered an essential component of sustainable agriculture. In this study, composite hydrogels with temperature/pH responsiveness were prepared by using modified attapulgite (ATP) as the inorganic filler and *N*-isopropylacrylamide (NIPAm) and sodium alginate (SA) as the temperature/pH-responsive monomer, and it was used as a carrier of urea to construct the hydrogel fertilizer. The results show that the addition of ATP modified by humic acid and hydrochloric acid to the hydrogel can significantly improve the hydrogel performance, and the hydrogel fertilizers prepared by using these two hydrogels as carriers have excellent environmental responsiveness and slow-release performances. The nutrient release behavior study showed that the hydrogel structure was more easily disrupted, and urea was released more rapidly under acidic and alkaline conditions. The network of the hydrogel collapses and shrinks at 30 °C, while urea was easily released from the hydrogel network. Compared to ordinary urea, the hydrogel fertilizer has an excellent slow-release performance. The environmentally responsive fertilizer would improve nutrient availability and avoid plant root damage and environmental pollution.

KEYWORDS: hydrogel, controlled release, urea, environmental responsiveness, green agriculture



1. INTRODUCTION

The global food system is under increasing pressure due to the ongoing increase in population and the unpredictability of the international environment, and agriculture is also dealing with significant difficulties.¹ Fertilizer is essential for maintaining and increasing food production;^{2–4} however, traditional fertilizer dissolves quickly after being applied to soil, and excessive fertilization not only damages plants but also causes many environmental problems. Slow-release fertilizers can release nutrients gradually but are unable to release nutrients in accordance with plant requirements and environmental factors such as the temperature and pH. The nutrient release rate is not synchronized with crop requirements, and improvement of the fertilizer utilization rate is still limited.^{5–7} Environmentally responsive fertilizers have gradually grown in popularity as a research topic in recent years due to their potential to address the dual issues of food security and environmental preservation.^{8,9} These fertilizers can control the release of nutrients in response to changes in the soil environment, allowing fertilizer release to be coordinated with the soil environment and crop nutrient uptake.¹⁰

Hydrogels can absorb and retain water, and when applied to soil, they improve the water retention capacity of soil.^{2,10} In addition to reducing evaporation losses, irrigation frequency, and environmental issues with fertilizer leaching, hydrogel-based fertilizers can also modulate nutrient release with environmental conditions through the shrinkage and swelling of structural networks.¹¹ A variety of materials may be used to create composite hydrogels, and hydrogels have promising future application possibilities in the area of new fertilizers. Zhang et al.¹² created a highly absorbent hydrogel by grafting a copolymer of acrylic acid and acrylamide (AA-co-AM) on a mulberry branch, which was subsequently loaded with urea to create an environmentally friendly slow-release urea fertilizer. Through ultraviolet irradiation copolymerization of acrylic acid monomer and coco peat cellulose in the presence of the cross-

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Scheme 1. Flowchart for the Preparation of Four Modified ATPs

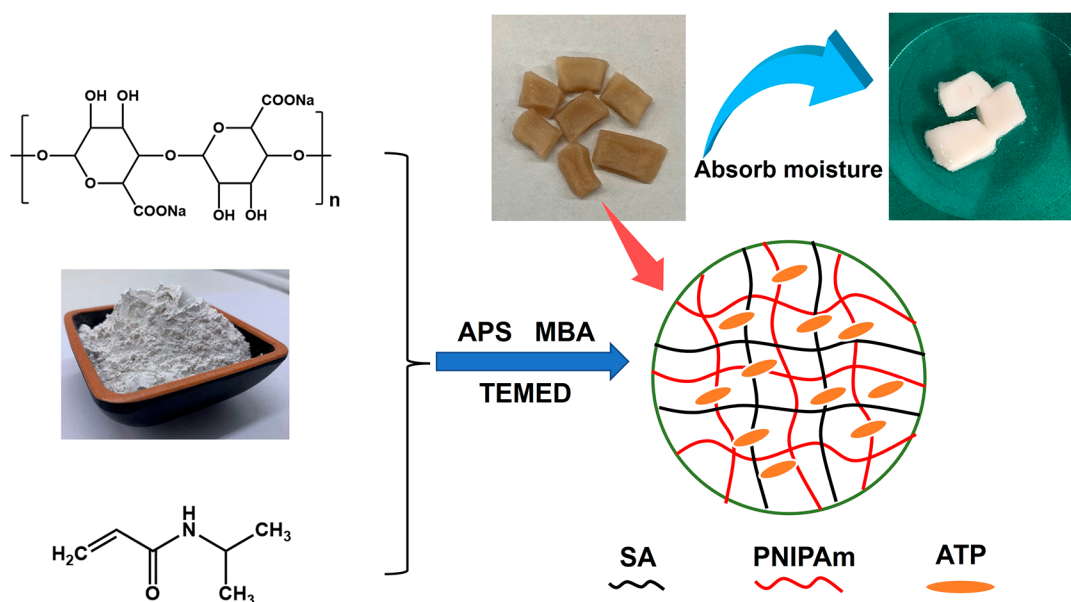
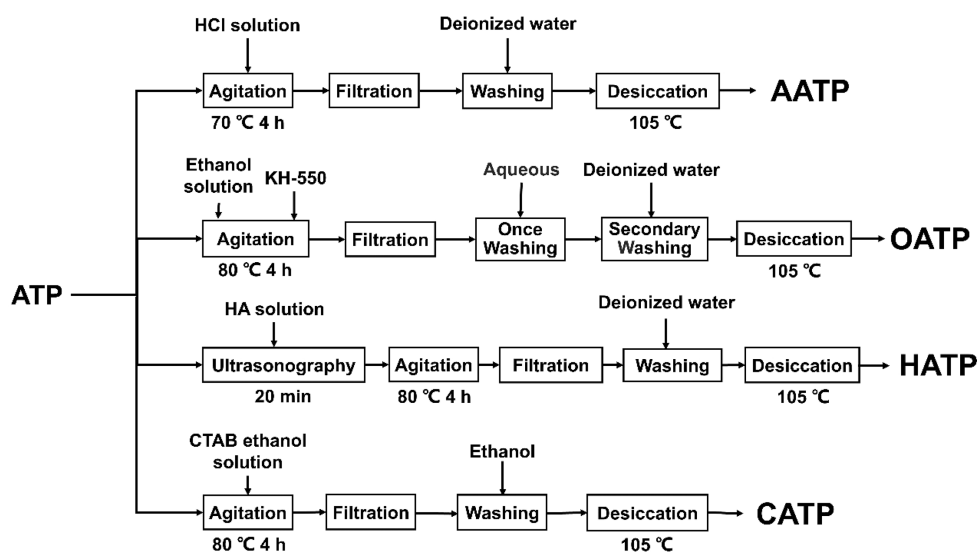


Figure 1. Schematic of the preparation of the SA/PNIPAm/ATP composite hydrogel.

linker trimethylolpropane trimaleate, Su et al.¹³ created a novel poly(acrylic acid)/coco peat (PAA/CP) superabsorbent composite hydrogel. Additionally, urea can be added to the PAA/CP hydrogel at a high loading.

It was discovered that adding temperature or a pH-responsive monomer could change the hydrogel swelling character and thus the release behavior of the loaded component. Liu et al.¹⁴ created poly(*N*-isopropylacrylamide/*N*-vinylpyrrolidone) [P(NIPAm/NVP)] hydrogels by *N*-vinylpyrrolidone (NVP) as the raw material and *N*-isopropylacrylamide (NIPAm) as the temperature-responsive monomer, which were then loaded with the medication doxorubicin. The results demonstrate that P(NIPAm/NVP) has excellent temperature-responsive characteristics. Xie et al.¹⁵ prepared the composite hydrogel CMCSSA with carboxymethyl chitosan sodium salt (CMCS) and the pH-responsive monomer sodium alginate (SA) and loaded the drug bovine serum albumin, and the results showed that CMCSSA has good pH responsiveness. The swelling performance of the

hydrogel could also be affected by structure modification with inorganic fillers. Liu et al.¹⁶ prepared an attapulgite (ATP)-based dual-responsive poly(*N*-isopropylacrylamide-*co*-acrylic acid) composite hydrogel by free-radical polymerization, as a result of ATP in the hydrogel network playing a supporting role, expanding the porosity of the hydrogel, and reducing the water molecule diffusion resistance, thus improving the performance of composite hydrogel swelling.¹⁶

Composite hydrogels with SA as the pH-responsive monomer and NIPAm as the temperature-responsive monomer have shown good application prospects in biomedical, food science, and agriculture fields.^{17–20} The mechanical characteristics and response time of composite hydrogels can be significantly enhanced by the addition of inorganic clay as a filler.^{16,21–23} In this work, SA, NIPAm, and modified ATP were used as raw materials to successfully prepare organic and inorganic composite hydrogels with dual temperature/pH-responsive characteristics, and the hydrogel fertilizer was constructed by using hydrogel as the carrier. The release

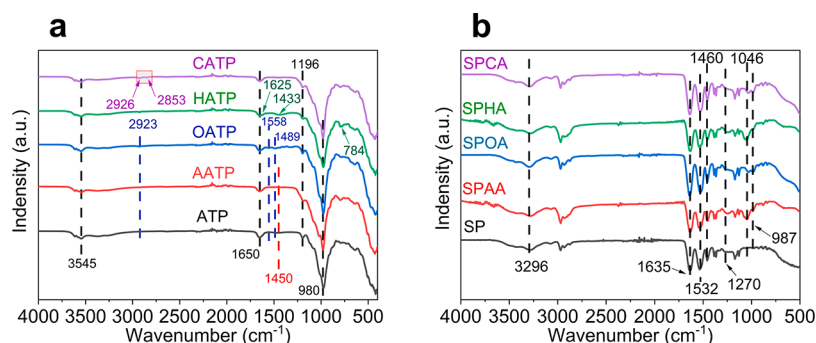


Figure 2. (a) FTIR spectra of the original ATP and four modified ATPs. (b) FTIR spectra of SP and a composite hydrogel.

behavior of urea from the hydrogel fertilizer in different environments was investigated. Also, the swelling kinetic curves of the composite hydrogels and the slow-release performance of the hydrogel fertilizers were studied to better evaluate the prepared composite materials.

2. MATERIALS AND METHODS

2.1. Reagents and Materials. Attapulgite (ATP) with a diameter of 100–120 nm and a surface area of 143.59 m²/g was obtained from Jiuchuan Technology Co. (Jiangsu, China). (3-Aminopropyl)-triethoxysilane (KH-550), humic acid (HA), cetyltrimethylammonium bromide (CTAB), anhydrous ethanol, and urea were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Shanghai Macklin Biochemical Technology Co., Ltd., supplied sodium alginate (SA), *N*-isopropylacrylamide (NIPAm), and tetramethylethylenediamine (TEMED). From Tianjin Kermel Chemical Reagent Co., Ltd., we obtained hydrochloric acid (HCl), *N,N'*-methylenebis(acrylamide) (MBA), and ammonium persulfate (APS).

2.2. Preparation of Modified ATP. HCl solution, KH-550, HA, and CTAB were used to modify ATP, respectively. Scheme 1 depicts a flowchart of the modification of ATP by various modifiers.^{24–26} The detailed modified experimental steps are shown in the Supporting Information (SI). AATP (HCl modified ATP), OATP (KH-550 modified ATP), HATP (HA modified ATP), CATP (CTAB modified ATP) are used to name modified ATPs.

2.3. Preparation of a SA/PNIPAm/ATP Composite Hydrogel. As illustrated in Figure 1, a hydrogel with both temperature and pH responsiveness was created by solution polymerization using NIPAm as the temperature-responsive monomer, SA as the pH-responsive monomer, and modified ATP as the inorganic additive material. The following preparation steps were followed, dissolving 0.94 g of NIPAm monomer and 0.06 g of SA in 5 mL of deionized water with continuous stirring. After complete dissolution, 0.02 g of the initiator APS, 0.02 g of the cross-linker MBA, and 0.02 g of modified ATP were added and thoroughly mixed with ultrasonic oscillation, after which 0.02 g of the accelerator TEMED was added and evenly stirred. After the reaction started, stirring was stopped and the beaker was sealed, and then the SA/PNIPAm/ATP composite hydrogel could be obtained.

The hydrogel was removed after 24 h of reaction at room temperature and cut into small pieces, and then it was submerged in deionized water for a predetermined amount of time. The deionized water was changed several times to flush out unreacted monomers. The hydrogel was vacuum-dried at 55 °C to a consistent weight, then sealed, and kept in storage. SP (composite hydrogel without ATP added), SPAA (composite hydrogel with AATP added), SPOA (composite hydrogel with OATP added), SPHA (composite hydrogel with HATP added), and SPCA (composite hydrogel with CATP added) are used to denote the several different types of hydrogels prepared.

2.4. Performance Evaluation of the SA/PNIPAm/ATP Composite Hydrogel. **2.4.1. Determination of the Maximum Water Absorption and Water Retention Performance.** The dry

hydrogel was packed into a dialysis bag and placed in a beaker, to which 200 mL of deionized water was added. The hydrogel was soaked at 20 °C for a certain amount of time to make it fully absorb water and swell to the saturated state, and excess water on the surface of the hydrogel was gently wiped off with filter paper. The mass of the hydrogel was weighed, and the maximum swelling capacity of the hydrogel could be obtained.

The material used for the water retention test was a hydrogel that absorbed water to saturation at 20 °C. Hydrogel saturated with water was placed in the surface dish, which was then placed in a blast drying oven at 40 °C. The hydrogel was taken out at regular intervals; the current swelling ratio (*Q*) was calculated by weighing it after excess water on the surface was wiped off, and the water retention performance curve of the hydrogels could be obtained. The formula for calculating the *Q* value is shown in the SI.

2.4.2. Determination of the Temperature- and pH-Responsive Performances. The dry hydrogels were placed in the dialysis bags and immersed in deionized water of different temperatures (20 and 30 °C). After swelling equilibrium, the hydrogels were weighed and the swelling ratio was calculated. Similarly, dry hydrogels were placed in dialysis bags and immersed in solutions of different pH values (3, 5, 7, 10, and 12) and weighed after swelling equilibrium, and the swelling ratio was measured.

2.5. Study on the Swelling Kinetics of the SA/PNIPAm/ATP Composite Hydrogel. The dry hydrogel was packed into a dialysis bag and later placed in a beaker containing deionized water at room temperature. At regular intervals, the hydrogel was taken out of the water, and any extra water was wiped off of the surface using filter paper. Then the hydrogel mass was measured, and the swelling ratio *Q* of the hydrogel was calculated at each instant.

2.6. Determination of the Nutrient Release Behavior of a Hydrogel Fertilizer. The hydrogels were loaded with urea by utilizing the swelling–adsorption and polymerization–embedding methods, respectively, to create the hydrogel fertilizers. The specific operation steps of the methods and the corresponding urea loading capacity calculation procedures are shown in the SI. The nutrient release behaviors of the hydrogel fertilizers were determined in solutions with different pH values (4, 7, and 9) and temperatures (20 and 30 °C), and the slow-release effects of the hydrogel fertilizer and large granular urea (4.20–4.25 mm in diameter) were also determined in deionized water at 20 °C. The SI displays the specific experimental methods. The urea content in aqueous solutions was determined using the spectrophotometric method of *p*-dimethylaminobenzaldehyde,²⁷ and in this paper, the fertilizer nutrient release curves were normalized.

2.7. Techniques of Characterization. The X-ray diffraction (XRD) of modified and original ATP was tested by using a Rigaku Corp. D/MAX-2200 X-ray diffractometer. The Fourier transform infrared (FTIR) of modified and original ATP was tested by a Nicolet iSSO FTIR spectrometer from Thermo Scientific. Thermogravimetric analysis (TGA) of the composite hydrogel was carried out using a Netzsch STA499F5 analyzer from room temperature to 600 °C at a heating rate of 10 °C/min under a dry nitrogen purge. The morphology of the composite hydrogel was observed by scanning

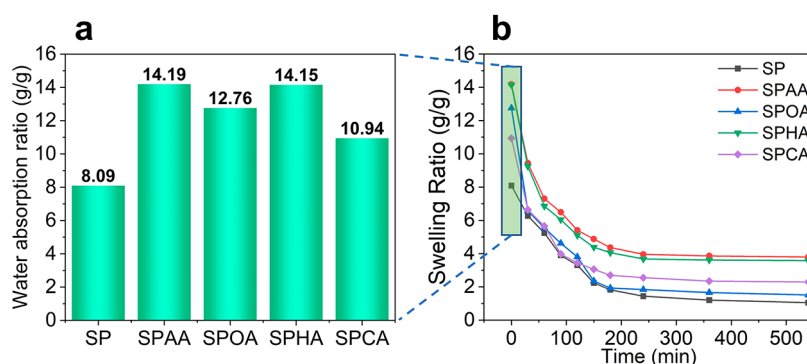


Figure 3. (a) Maximum swelling ratio of a hydrogel in deionized water at 20 °C and (b) water retention performance at 40 °C.

electron microscopy (SEM; TESCAN MIRA4). The release performance of urea from the hydrogel fertilizer was tested by a NanBei T9 ultraviolet spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of Modified ATP and Composite Hydrogel. From Figure 2a, it can be seen that the characteristic peaks of ATP exist at 3545, 1650, 1196, and 980 cm^{-1} , where the absorption peak at 3545 cm^{-1} is from the stretching vibration of (Al,Mg)-OH, the absorption peak at 1650 cm^{-1} is attributed to the bound water adsorbed in ATP, the vibration around 1196 cm^{-1} is ascribed to the bending vibration of Si-O-Si, and the absorption peak at 980 cm^{-1} is caused by the stretching vibration of Si-O. Meanwhile, a comparison between ATP and AATP shows that the intensity of the peak gradually decreases at 1196 cm^{-1} , which proves that HCl breaks part of the Si-O bond and activates the ATP surface. Because carbonate impurities were greatly reduced following acid treatment, AATP lost its absorption peak at 1450 cm^{-1} , which is the vibrational absorption peak of carbonate.^{28,29} The FTIR spectrum of OATP reveals that the compound generated additional absorption peaks at 1489, 1558, and 2923 cm^{-1} . The absorption peaks produced at 2923 and 1489 cm^{-1} are the bending and stretching vibrational peaks of the C-H bond on the KH-550 carbon chain, which indicates the grafting of organic groups on the surface of ATP;²⁶ the absorption peak at 1558 cm^{-1} is from the bending vibrational peak of $-\text{NH}_2$. HATP exhibits two new absorption peaks, one at 1624 cm^{-1} for the stretching vibration of C=O on the benzene ring and the other at 2928 cm^{-1} for the asymmetric vibration of the C-H bond in the long carbon chain of HA, indicating a chemical reaction between HA and ATP.³⁰ The effective surface modification of ATP by CTAB is indicated by the appearance of new distinctive peaks in CATP at 2926 and 2853 cm^{-1} , which are related to the C-H stretching vibrations of the methyl group of CTAB;³¹ a partially enlarged view of the CATP curve can be seen in Figure S1.

In Figure 2b, the O-H bond in SA has a bending vibrational peak that can be seen as an absorption peak at 3296 cm^{-1} . Compared to the curve of SP, which corresponds to the distinctive absorption peaks of Si-O of ATP, the other composite hydrogels more clearly demonstrate absorption peaks at 1046 and 987 cm^{-1} , demonstrating the successful addition of modified ATP to the hydrogel system. The amide group in NIPAm exhibits C=O stretching and bending vibrational peaks at 1635 and 1532 cm^{-1} , respectively, while the C-N bond exhibits a bending vibrational peak at 1460

cm^{-1} . The aforementioned experimental findings show that the composite hydrogel was successfully manufactured.

3.2. Water Absorption and Water Retention Performances of the SA/PNIPAm/ATP Composite Hydrogel.

Figure 3a shows that SPAA has the highest water absorption ratio because acid modification effectively removes impurities from ATP, increases its specific surface area and pore volume, and increases the number of active adsorption sites on the surface, all of which can enhance its ability to absorb water.³² Additionally, SPHA had a high water absorption ratio because of the adsorption of HA on the surface of ATP, and HATP may improve the ability of the hydrogel to absorb water due to the many hydrophilic groups of HATP. In addition, the water absorption performance of SPOA is improved because the silane coupling agent can graft hydrophilic groups to the surface of ATP. The surface active agent can improve the binding force of the ATP and SA hydrogel and promote better compounding between them, so the water absorption of SPCA is also improved. Compared to SP, the water absorption abilities of SPAA, SPOA, SPHA, and SPCA were increased by 75.4%, 57.8%, 75.0%, and 35.2%, respectively.

The water retention performance of the composite hydrogel was superior to that of SP after the addition of ATP, as shown in Figure 3b. Among them, the water retention performance of SPAA was the best, with a water absorption ratio of 3.96 g/g at 240 min, which was significantly higher than that of the SP hydrogel at 240 min of 1.44 g/g and represented a performance improvement of about 175%. Meanwhile, the water retention performances of SPHA, SPOA, and SPCA were all improved to different degrees compared to that of SP. The reason for the substantial improvement in the water retention performance is that the addition of modified ATP, with its special structure combined with the three-dimensional network system of the hydrogel, makes the gel cross-link more tightly, so the ability to retain water is enhanced. The water retention performances of SPAA and SPHA are superior, mainly because of more hydrophilic groups exposed on the surface of AATP and HATP, and their addition to the hydrogel enhances the binding ability of the system to water molecules.

Meanwhile, combined with TGA (Figure S2), it can be seen that all four composite hydrogels have good thermal stability. The good thermal stability makes the composite hydrogel an excellent carrier for fertilizer because it ensures that the hydrogel fertilizer will not decompose and fail under direct sunlight or other high-temperature conditions.

3.3. Temperature- and pH-Responsiveness Analysis of the SA/PNIPAm/ATP Composite Hydrogel. The equilibrium swelling ratios of SP and all modified ATP

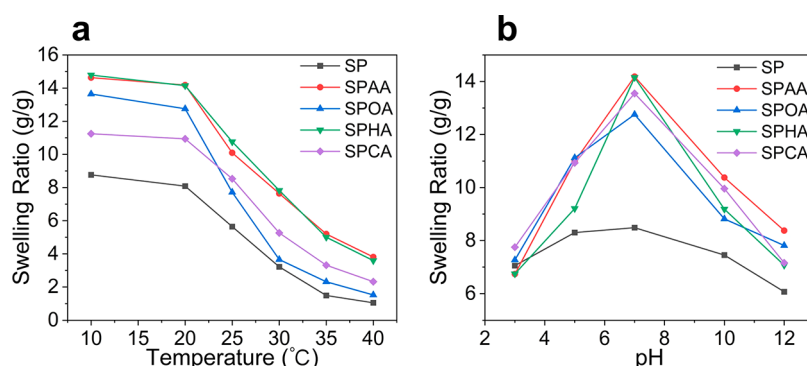


Figure 4. Equilibrium swelling ratio of the SA/PNIPAm/ATP composite hydrogel changes with (a) temperature and (b) pH.

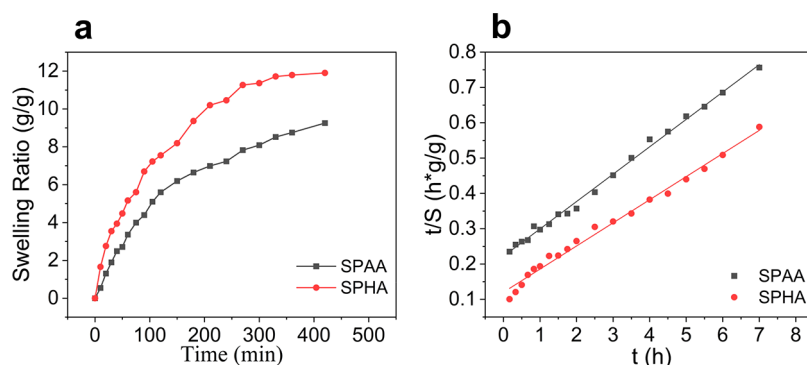


Figure 5. (a) Swelling curves of SPAA and SPHA in water and (b) the t/S –time relationship of SPAA and SPHA during the process of swelling in water.

composite hydrogels displayed a trend of decreasing with temperature, as indicated in Figure 4a, and the decreasing rate was accelerated at about 20 °C. The equilibrium swelling ratio of the hydrogel did not significantly change at low temperatures, while it significantly decreased at high temperatures. The hydrophilic and hydrophobic groups in PNIPAm control how responsive hydrogels are to temperature. When the external temperature is lower than the lower critical solution temperature (LCST) of the composite hydrogel, hydrogen bonding occurs between the hydrophilic groups in the polymer network and water molecules, and the hydrogel molecular chains are in a diastolic state, so it absorbs water and swells.^{33,34} However, as the temperature rises, the interaction between hydrophobic groups in the hydrogel system strengthens; when the external temperature is higher than the LCST of the hydrogel, the polymeric network of the hydrogel curls up and aggregates due to the interaction between hydrophobic groups, the network of hydrogel undergoes a structure transition, and the swelling degree decreases sharply.¹⁸

As can be seen from Figure 4b, the equilibrium swelling ratio of composite hydrogels with the addition of modified ATP tends to increase and then decrease with an increase of the pH, and the equilibrium swelling ratio is at its maximum at pH = 7. The obvious pH responsiveness of hydrogels is due to the dissociation of $-\text{COO}^-$ from SA molecules under acidic conditions, which will combine with H^+ to form $-\text{COOH}$ and hydrogen bonding with $-\text{CO}-\text{NH}-$ in PNIPAm, resulting in contraction of the hydrogel network.³⁵ When the pH is close to neutral, $-\text{COOH}$ dissociates to the maximum degree, the molecular chain can be fully extended, and the hydrogel water absorption ratio is the best.^{34,36,37} When the pH of the solution

increases to alkaline, the ionic strength in the hydrogel network increases, so that the residual charge on the main chain of the hydrogel is gradually shielded by counterions, resulting in the contraction of macromolecular chain segments, and therefore the swelling degree decreases.³⁸ The responsiveness of the composite hydrogel to temperature and pH was unaffected by the addition of modified ATP, and the equilibrium swelling curve trend of the SA/PNIPAm/ATP composite hydrogels with respect to the temperature or pH was essentially the same as that of SP.

3.4. Swelling Kinetics of the SA/PNIPAm/ATP Composite Hydrogel. The swelling kinetic equations can be studied to quantify the water absorption performance of hydrogels, and because fertilizer loading and release are inextricably linked to the water absorption performance of hydrogels, the swelling kinetic equations can help to better analyze the nutrient release of hydrogel fertilizer. In general, for water-soluble nutrients, if the hydrogel has been immersed in a large and sufficient amount of water, the release of nutrients from a hydrogel with a high swelling rate will be relatively fast because a large amount of water will enter the hydrogel in a short amount of time, and the nutrients will be dissolved and exchanged with external water rapidly.³⁹ However, in practice, most rainfall washouts do not cause soil flooding, and hydrogels with better water retention properties tend to hold more nutrients because water can be completely immobilized by the hydrogel, and nutrients are not lost with the water. Therefore, we selected SPAA and SPHA for subsequent kinetic and loading fertilizer studies, but this does not mean that SPOA and SPCA do not have potential as fertilizer carriers but only that we focused on the former due to space limitation.

A Scott swelling kinetic model was used to study the swelling process of composite hydrogels; this is shown in eqs 1 and 2. The swelling curves of the two hydrogels in water are shown in Figure 5a. The three successive processes of water diffusion into the hydrogel, polymer structure relaxation, and polymer chain stretching in water are typically what cause reticular structured hydrogels to swell.⁴⁰ When $t \leq 105$ min, the hydrogel absorbs water faster at the beginning of the swelling time, and the slope of the curve is larger and approximately linear; with extension of the swelling time, when $105 \text{ min} \leq t \leq 320$ min, the growth trend of the curve slows, and the water absorption rate of the hydrogel decreases; at ≥ 320 min, the mass of the hydrogel increases more slowly and finally tends to be unchanged, and the hydrogel is saturated with water and tends to swelling equilibrium.

$$\frac{dS}{dt} = K_s(S_\infty - S)^2 \quad (1)$$

$$\frac{t}{S} = A + Bt \quad (2)$$

In the two equations, t represents the time that the hydrogel is immersed in water (min), S represents the water absorption capacity of hydrogel (mg), S_∞ represents the maximum water absorption capacity of the hydrogel (mg), and K_s represents the swelling rate constant of hydrogel (g/g/h). In eq 2, $A = \frac{1}{K_s S_\infty^2} = \frac{1}{(dt/dS)^0}$, A represents the inverse of the swell rate (t/S) of the initial phase of the hydrogel and $B = 1/S_\infty$. t/S was calculated based on the obtained data, a t/S -time relationship graph was made, and the results are shown in Figure 5b.

Table 1 displays the variables relating to the swelling of SPAA and SPHA in water. The fitted values of the theoretical

Table 1. Relevant Parameters of SPAA and SPHA during the Whole Process of Swelling in Water

sample	A	B	S_∞	K_s
SPAA	0.231	0.075	13.277	0.025
SPHA	0.120	0.065	15.279	0.036

maximum water uptake S of the hydrogels are reasonably close to the measured values.

3.5. Microscopic Analysis of the Hydrogel Structure.

It can be clearly seen from Figure 6 that the interiors of the hydrogels are irregular, loose, and porous networks that are alternately connected. The surface of SPAA is smoother than that of SPHA, and the surface of SPHA is more uneven. SPHA has a larger specific surface area relative to SPAA, and hydrophilic groups are exposed more, thus increasing the utilization of hydrophilic groups to water during the water absorption process.⁴¹ As can be seen from the XRD spectra in Figure S3, the structure of ATP was not altered by either HCl solution modification or HA modification. Acid treatment is more about unclogging the pore channels and increasing the surface area to enhance the adsorption capacity of ATP.²⁶ The positions of the diffraction peaks before and after HA modification were essentially unchanged, with only the relative intensity of the low-angle diffraction peak of HATP changing. The reason is that the HA molecule is adsorbed onto the ATP surface through hydrogen bonding and has not yet entered the ATP interlayer, which has no effect on the crystal structure. However, HA is wrapped around the ATP surface, thus reducing the diffraction peak intensity.

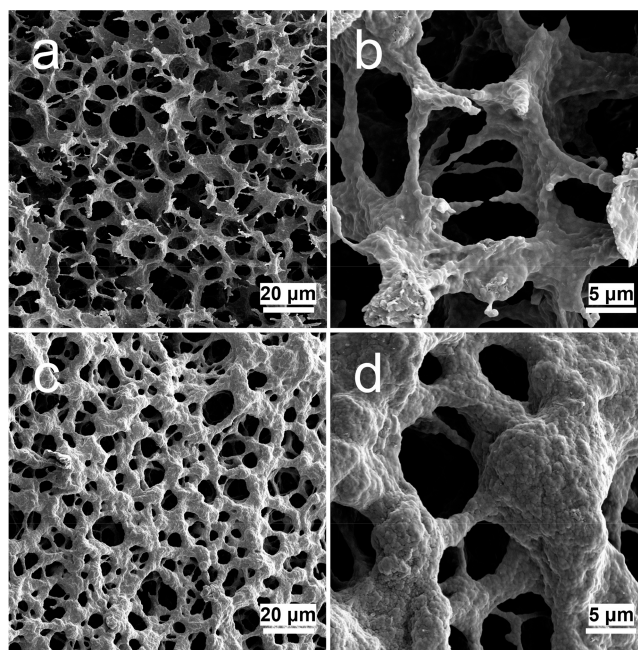


Figure 6. SEM morphology of (a and b) SPAA and (c and d) SPHA composite hydrogels.

Because HA is present on the surface of ATP, the large number of hydrophilic functional groups contained in HA is well retained during polymerization without being entangled in the molecular chain. SPHA has a rich porous structure and a larger specific surface area, and the hydrophilic groups on its surface can absorb a large amount of water in a short time; therefore, its swelling rate is faster. This also explains why SPHA has a faster swelling rate than SPAA in the initial stage and a much larger swelling rate constant K_s than SPAA.

3.6. Nutrient Release Behavior of the Hydrogel Fertilizer. **3.6.1. Environmentally Responsive Nutrient Release Behavior of Urea at Different pH and Temperature Values.** Four hydrogel fertilizers, SPAA-U(S), SPAA-U(P), SPHA-U(S), and SPHA-U(P), were produced by using SPAA and SPHA, respectively, loaded with urea, where S stands for the swelling-adsorption method and P stands for the polymerization-embedding method.

Parts a and b of Figure 7 indicate that the hydrogel fertilizers have an excellent stimuli-responsive release behavior according to the pH in water, and the nutrient release rate under acidic or alkaline environments is faster than that under a neutral environment, which is because the polymer network collapses severely under acidic and alkaline conditions, the force of interaction with urea is reduced drastically, and the nutrients flow out of the hydrogel system. For instance, the cumulative nutrient release rate of SPHA-U(S) was 66.1%, 94.6%, and 94.1% after 24 h in solutions with pH values of 7, 9, and 4, respectively.

When parts c and d of Figure 7 are compared, it can be seen that the nutrient release of hydrogel fertilizer has significant temperature responsiveness. The nutrient release time of hydrogel fertilizer was longer at 20 °C than at 30 °C. For example, the cumulative nutrient release of SPAA-U(P) and SPHA-U(P) was 63.63% and 66.7%, respectively, when immersed in water for 24 h at 20 °C, while the cumulative release of both was 70.77% and 73.26% at 30 °C. This was mainly because when the temperature increased from 20 to 30

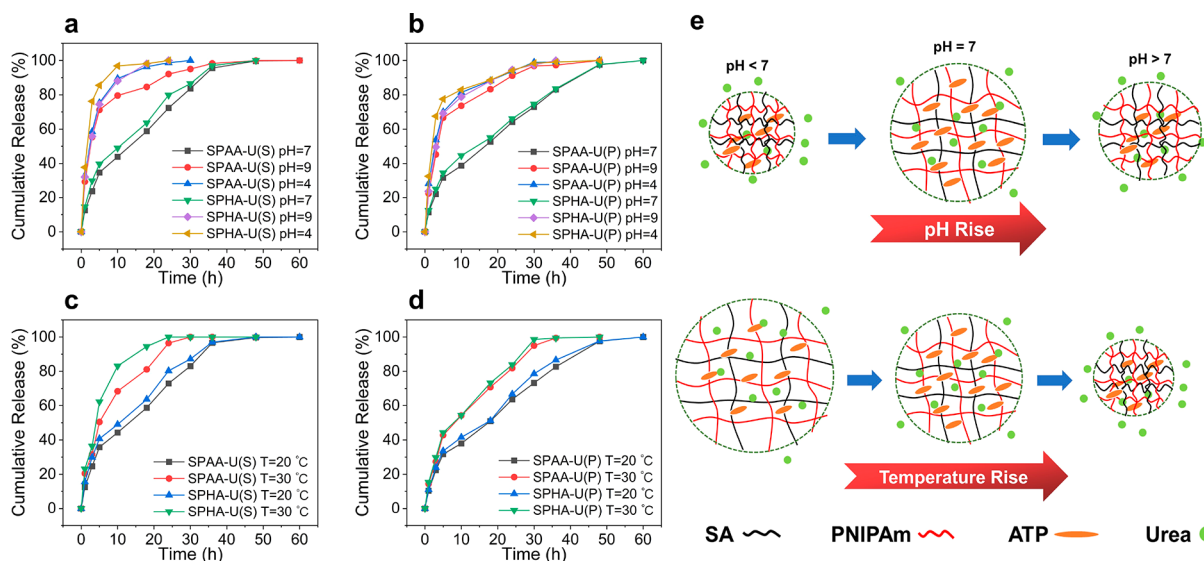


Figure 7. Cumulative release of nutrient from the (a) swelling–adsorption method and (b) polymerization–embedding method of hydrogel fertilizer under different pH conditions. Cumulative release of nutrient from the (c) swelling–adsorption method and (d) polymerization–embedding method of hydrogel fertilizer under different temperature conditions. (e) Schematic diagram of nutrient release from hydrogel fertilizer at different pH and temperature values.

°C, the polymer network of the hydrogel collapsed and contracted with an increase of the temperature, the water absorption ability decreased, and the interaction force between urea molecules and the hydrogel network weakened, while urea was easily released under the effect of the collapse and contraction of the hydrogel network.⁴²

The trend of a fast and then slow nutrient release rate of hydrogel fertilizer is because when water molecules first enter the hydrogel system, the polymer structure is relaxed, the binding force on urea molecules is reduced, and the nutrient release rate is faster, and then as the swelling rate of hydrogel slows, the movement of water molecules tends to dynamic equilibrium, so the dissolution rate of urea from the hydrogel system slows.⁴³ In addition, the slow-release performance of SPHA fertilizer under the same conditions is poorer than that of SPAA fertilizer. This is due to the presence of a large number of hydrophilic groups on the surface of HATP, which has a strong ability to bind to water molecules; SPHA obtained by adding to the hydrogel swells faster and the nutrients flow more easily with water, so the SPHA-U(S) and SPHA-U(P) nutrients are released faster.⁴⁴ The changes in the polymer network structure and nutrient release behavior concerning the pH and temperature are listed in Figure 7e.

The swelling kinetic parameters of the two hydrogels showed that SPHA had a higher swelling rate. In the previous section, we mentioned that urea, as a water-soluble nutrient, can be dissolved and released into the environment quickly after water enters the hydrogel. It is worth mentioning that the nutrient release rate of the hydrogel fertilizer prepared by polymerization–embedding was slower than those of the fertilizers made by swelling–adsorption because the urea molecules were wrapped into the more densely wound sites of the hydrogel macromolecular chains during the polymerization reaction, so the nutrient release rate was slightly slower.

3.6.2. Comparison of the Slow-Release Performance of a Hydrogel Fertilizer and Large Granular Urea. As can be seen from Figure 8, the nutrient of ordinary large particle urea was completely released in less than 2 h in deionized water, while

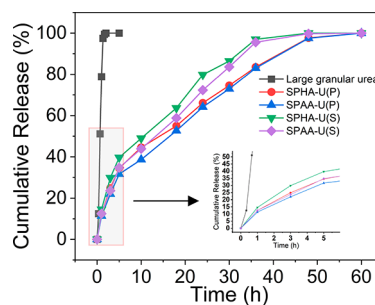


Figure 8. Comparison of the slow-release performances of the hydrogel fertilizer and large granular urea.

the hydrogel fertilizer had less than 20% of its nutrients released at 2 h. Overall, the slow-release time of urea was increased by about 30 times, which shows that the hydrogel fertilizers have excellent slow-release ability.

4. CONCLUSION

By the addition of modified ATP to the polymer matrix and using SA and NIPAm as the environmentally responsive monomers, composite hydrogels with dual responsiveness were created in this work. The water absorption and water retention performances, pH and temperature responsiveness, and thermal stability of the composite hydrogels were systematically evaluated. Besides, the composite hydrogels with better performances were compounded with fertilizer urea by swelling–adsorption and polymerization–embedding methods to obtain hydrogel fertilizers; the nutrient release pattern of hydrogel fertilizer under different temperature and pH conditions was investigated. As a result of ATP modification, the hydrogel employed in this work greatly increased the water absorption ability, improved the water retention ability, and had a swelling kinetics that was consistent with that of the Scott model. Additionally, the composite hydrogels exhibit multiple responsiveness to temperature and pH, and the swelling ratio decreases with increasing temperature and increases but then decreases with increasing pH. Hydrogels

loaded with urea still exhibit environmental responsiveness and have a good slow-release capability compared to ordinary urea.

The composite hydrogels and hydrogel fertilizers prepared in this work can provide a valuable strategy for the creation of numerous stimulus-responsive green fertilizers and promote the modernization of agriculture to a certain extent.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.3c02018>.

Additional experimental details about this study and characterization analysis (PDF)

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J.W.: conceptualization, methodology, investigation, visualization, and writing—original draft. H.Y.: methodology, investigation, visualization, and writing—original draft. C.H.: visualization, writing—review and editing, and funding acquisition. H.G.: visualization, investigation, and writing—review and editing. S.G.: conceptualization and project administration. Y.Y.: conceptualization, visualization, and writing—review and editing. H.J.: conceptualization, visualization, and writing—review and editing. Y.W.: methodology and investigation. M.W.: conceptualization and project administration.

Notes

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