


Cite this: *RSC Adv.*, 2024, 14, 14758

Received 9th February 2024
Accepted 20th March 2024

DOI: 10.1039/d4ra01021c

rsc.li/rsc-advances

Swelling behaviors of superabsorbent composites based on acrylic acid/acrylamide copolymer and acid-modified attapulgite

Hanru Ren,^{*ab} Jun Ren,^{ab} Ling Tao^{ab} and Xuechang Ren^a

The swelling behaviors and water retention of superabsorbent materials prepared from acrylic acid/acrylamide copolymer and acid-modified attapulgite under ultrasonic treatment and different pH conditions were investigated. The results demonstrated that a suitable amount of attapulgite can effectively improve the absorption capacity. The superabsorbent achieved the highest absorptions of 1257.54 g g⁻¹ and 209.45 g g⁻¹ in distilled water and a 0.9 wt% NaCl solution, and a higher water absorbency occurred over a wide pH range of 5–9 when the ultrasonic power was 200 W, and the attapulgite content was 10%. Addition of attapulgite could significantly increase the water absorption and retention of this kind of material, which can be applied as a sand-fixing material.

1. Introduction

Sand-fixing materials (SFMs) have been suggested as a solution for controlling desertification in arid and semiarid regions because they could influence the configuration and function of the desert surface by enhancing soil stability and increasing moisture retention. Superabsorbent polymers are always major components of SFMs since they can absorb and retain huge amounts of water or aqueous solution and are difficult to remove, even under high pressure or temperature.^{1,2} Superabsorbent composites have a three-dimensional network structure of crosslinked hydrophilic polymer. Because of their unique properties, such as ability to swell, insolubility and hydrophilicity, applications of superabsorbent materials have been expanded to diverse fields, such as agriculture, horticulture, and environmental protection. The preparation methods and swelling behaviors of superabsorbent composites have attracted considerable attention from many researchers;^{3–7} however, most superabsorbents are expensive and environmentally toxic. Hence, to reduce the cost of production and improve biocompatibility, renewable, eco-friendly, non-toxic, biodegradable, natural organic materials, such as starch, sodium alginate, chitosan, guar gum and inorganic clay minerals, are often introduced into the synthesis process of superabsorbent composites.^{8–12}

Superabsorbent composites containing organic–inorganic minerals have received extensive attention. Attapulgite is a type of magnesium aluminum silicate clay mineral. A large number of hydrophilic Si–OH bonds are present on the surface of

attapulgite, each of which could undergo a graft copolymerization reaction with a hydrophilic vinyl monomer, and graft copolymerization occurs between hydrophilic vinyl monomers. When attapulgite was added to resins, it improved the salt tolerance and absorbent properties of newly formed composite materials and also effectively reduced the production cost.^{8,13–18} The new material formed by copolymerization grafting of attapulgite with acrylamide monomers and 2-acrylamido-2-methylpropanesulfonic acid has strong anionic traits, salt resistance, and water absorption.¹⁹ In addition, it has saline alkali tolerance, and when added into high-water-absorbency polymer materials, it could not only improve the absorbency, salt tolerance and other properties of the materials but also effectively reduce the production cost, so it is suitable for preparing inorganic–organic composite superabsorbents.^{20–22}

Considering the strong impact of attapulgite on the properties of corresponding superabsorbent composites, a composite superabsorbent was prepared by grafting hydrophilic monomer acrylic acid and acrylamide onto acid-modified attapulgite clay in aqueous solution. Potassium persulfate was used as the initiator and *N,N*-methylenebisacrylamide was used as a crosslinker. The acid-modified attapulgite was incorporated into the polyacrylamide polymeric network to investigate its effects in terms of the swelling behaviour, pH-sensitivity, salt-resistance properties and water retention of the superabsorbent composites. Increasing the proportion of attapulgite clay in the material preparation process is more conducive to bonding between the material and desert surface and helps to form a soil biocrust, achieving the goal of biological sand fixation. Sand-fixing materials synthesized with resins and attapulgite are explored under attapulgite addition and ultrasonic treatment.

^aSchool of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P. R. China. E-mail: renjun@mail.lzjtu.cn

^bGansu Hanxing Environmental Protection Co. Ltd, Lanzhou 730070, China



2. Materials and methods

2.1. Materials

Attapulgite clay was obtained from Linze county of Gansu province, China. The main composition was as follows: SiO₂, 63.47%; Al₂O₃, 18.01%; MgO₄, 20%; Fe₂O₃, 5.16% and K₂O, 3.64%. It contains mineral impurities, such as attapulgite, quartz, dolomite and montmorillonite (Fig. 1). Acrylic acid (AA), acrylamide (AM), potassium persulfate, *N,N*-methylenebisacrylamide (MBA), sodium hydroxide (NaOH) and sodium bisulphite were all of analytical grade. In electron microscope images, the rod-shaped structure of attapulgite is very obvious, and it is connected with other crystal minerals and amorphous silicates, consistent with the characteristics of clay minerals in terms of adhesion and cementation (Fig. 1).

2.2. Acid-modified treatment of attapulgite

First, 10 g of attapulgite clay was soaked in 4 mol L⁻¹ H₂SO₄ solution at a temperature of 25 °C for 72 hours, and then, the material was washed with distilled water to a pH of 7 and placed in an oven at a temperature of 105 °C to dry. A certain amount of NaOH was added to distilled water in a beaker, and then, a certain amount of AA was slowly added to the beaker. During this process, the beaker was placed in an ice-water bath. The degree of neutralization was maintained at 80%. A pre-determined amount of AM was added into the beaker with

vigorous stirring to produce the monomer solution. Based on the performance the adsorbents were prepared by the addition of acrylic acid and acrylamide,^{7,12,18} where AA and AM were added according to the mass ratio 15.0 : 4.0. A variable amount of acid-modified attapulgite, and later, 30 mL of distilled water were added to a beaker with vigorous stirring to produce acid-modified attapulgite.

2.3. Synthesizing experiment

First, 5 g of NaOH was first dissolved in 10 mL of distilled water in a beaker. Then, 15 mL of AA was slowly added to the NaOH solution, and the resultant solution was neutralized in an ice-water bath with a neutralization degree of 80%. Further, 15 mL of AA and 4 g of AM were then added to the neutralized solution to prepare a monomer solution. Acid-modified attapulgite samples with different mass fractions of 0%, 3%, 5%, 8%, 10%, and 15% (denoted ATP0, ATP3, ATP5, ATP8, ATP10, and ATP15, respectively) were taken and dissolved in 30 mL of distilled water to prepare attapulgite colloids. In addition, the amount of *N,N*'-methylene bisacrylamide (acting as the cross-linker) was 0.05%, and the dosage of potassium persulfate and sodium bisulfite (molar ratio = 1 : 1; acting as the reaction initiator) was 0.6%. *N*'-methylene bisacrylamide, potassium persulfate, and sodium bisulfite were dissolved in 10 mL of distilled water to prepare an initiator-crosslinker solution (Table 1). The temperature of the water bath was set to 80 °C.

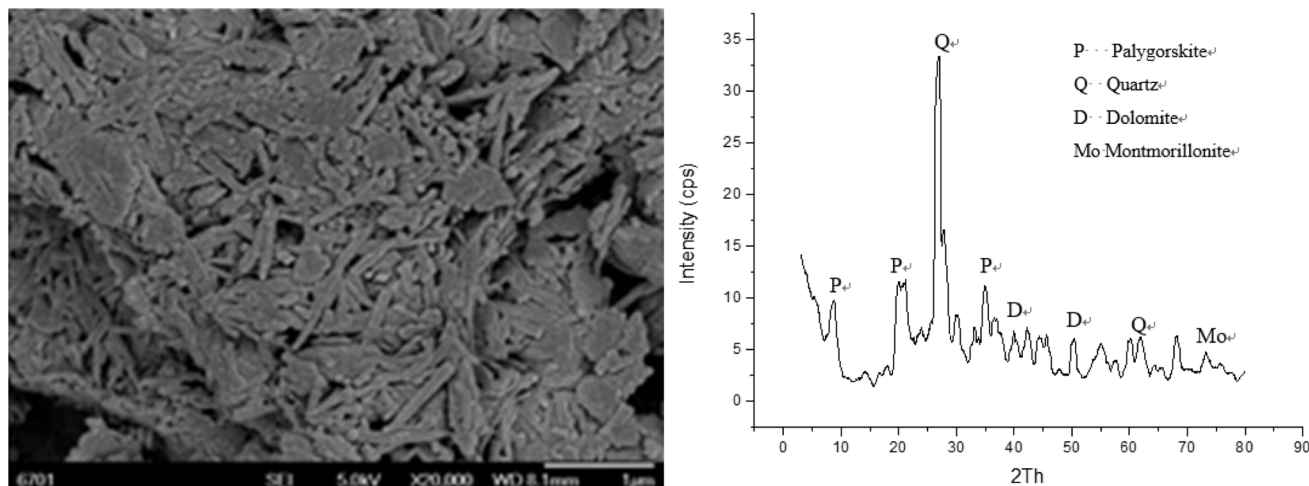


Fig. 1 SEM image and XRD pattern of attapulgite.

Table 1 Proportions (%) of prepared materials for the preparation of sand-fixing materials

Material	ATP0	ATP3	ATP5	ATP8	ATP10	ATP15
Acid-modified attapulgite	0%	3.00%	5.00%	8.00%	10.00%	15.00%
AA	77.30%	74.98%	73.44%	71.12%	69.57%	65.71%
AM	9.80%	9.50%	9.31%	9.02%	8.82%	8.33%
Potassium persulfate	0.17%	0.17%	0.16%	0.16%	0.15%	0.14%
Sodium bisulfite	0.43%	0.42%	0.41%	0.40%	0.39%	0.37%
NaOH	12.25%	11.88%	11.64%	11.27%	11.03%	10.41%
<i>N,N</i> '-Methylene bisacrylamide	0.05%	0.05%	0.05%	0.05%	0.05%	0.04%

Until the temperature reached the specified value, the attapulgite colloids and initiator-crosslinker solutions were added to the monomer solution. After the reaction, the obtained product was crushed and washed with aqueous ethanol, then dried at 90 °C in an oven and ground to 100 mesh to obtain the sand-fixing materials.

2.4. Ultrasonic treatment

The beaker with the acid-modified attapulgite was put into an ultrasonic reaction device with a variable amount of ultrasonic power (200 W, 300 W, 400 W, or 500 W) and heated at 80 °C. The monomer solution and initiator-crosslinker solution were added into the beaker with stirring. Approximately 10 min later, the product was washed several times with water and alcohol (1 : 9 in volume) to remove any unreacted reactants. The product was dried in an oven at 90 °C until the weight of the product was constant. The product was crushed to a particle size of 100 mesh to obtain the sand-fixing materials under ultrasonic treatment.

2.5. Measurement of swelling properties

First, 0.5 g of dried sample was mixed with 800 mL of distilled water in a beaker. The water absorption rate (WAR) and saline absorption rate (SAR) were calculated with eqn (1) and (2):

$$\text{WAR} = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (1)$$

$$\text{SAR} = \frac{(M_2 - M_1)}{M_1} \times 100\% \quad (2)$$

where M_1 is the mass of the sand-fixing material before swelling (g), and M_2 is the mass of the sand-fixing material after swelling (g).

Further, 0.5 g of sample was weighed and put into a container. The container was kept in a constant-temperature oven at 90 °C after saturation. The container was taken out of the oven at a certain time interval and weighed. The water retention rate (WRC) was calculated with eqn (3):

$$\text{WRC} = \frac{W_2}{W_1} \times 100\% \quad (3)$$

where W_2 signifies the mass after dehydration (g), and W_1 denotes the mass after saturation with water (g). Then, 0.5 g of sample was further added to 500 mL of distilled water, and 0.1 M HCl or NaOH was used to adjust the initial pH value of the resultant solution. Five treatments of pH 6–10, were shaken at room temperature for 2 h until the sand-fixing materials reached equilibrium for swelling. The influence of pH change on water absorption rate was examined.

2.6. Statistical analysis

Two-way analysis of variance (ANOVA), followed by a multiple-comparison test (Duncan's test), was used to analyze differences among treatments; all treatments had six repetitions.

3. Results and discussion

3.1. Effect of attapulgite addition on water absorbency

The ratio of attapulgite to resins determined the absorbent performance when attapulgite was used as a comonomer for the synthesis of sand-fixing materials. The influence of attapulgite on water absorbency was investigated by varying the mass ratio from 3% to 15%. The addition of attapulgite obviously enhanced the water absorbency of the sand-fixing materials. The water absorbency increased with the addition of attapulgite. The addition of attapulgite could enhance the water absorbency, and when 10 wt% of attapulgite was added, the WAR for distilled water and saline absorption rate reached maxima of 955.36 g g⁻¹ at 80 min and 91.47 g g⁻¹ at 60 min, respectively (Fig. 2 and 3).

This result may be because attapulgite was easily dispersed into the polymeric gel and enhanced its hydrophilicity, and attapulgite participated in the construction of a three-dimensional hydrophilic network through its active -OH groups reacting and crosslinking with polymeric chains. Attapulgite nanoparticles can alleviate the entanglement of grafted

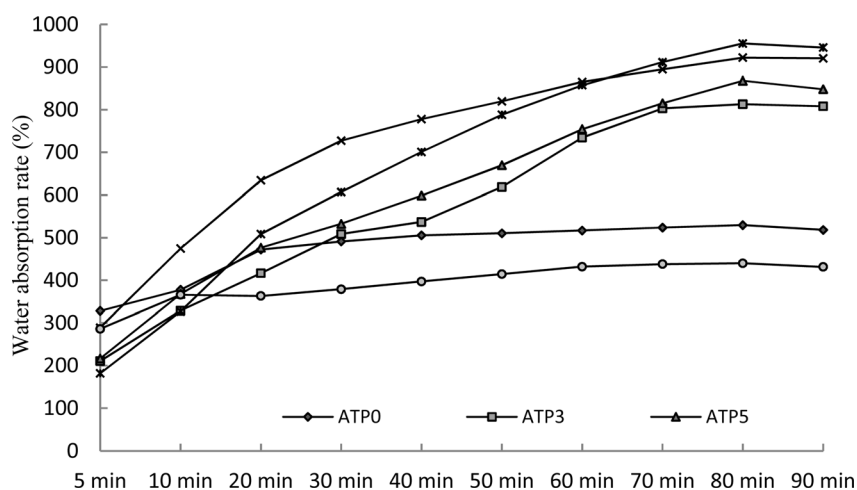


Fig. 2 Water absorption rate of sand-fixing materials synthesized with polymer and acid-modified attapulgite for distilled water.



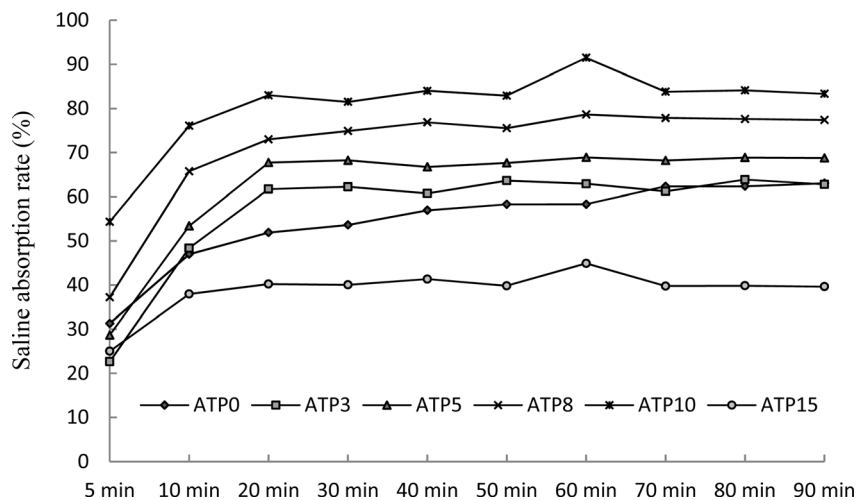


Fig. 3 Saline absorption rate of the sand-fixing materials for salt solution (0.9 NaCl).

polymer chains and weaken the hydrogen bonding interaction between -COOH groups, thereby reducing the degree of physical crosslinking and promoting the formation of a polymer network structure.^{23,24} With higher attapulgite addition (15%), water absorbency was remarkably reduced, because the attapulgite nanoparticles may become key crosslinking points in the polymers. Increasing the amount of attapulgite may cause a higher density of crosslinking and network space, making it difficult for water molecules to penetrate and gradually reducing water absorption. Conversely, an excessive amount of attapulgite may fill the physical space of the network, reduce the proportion of hydrophilic groups per unit volume, and lead to a decrease in the hydrophilicity of the composite material and cause a diminishment in water absorbency. This may be because attapulgite is combined with the polymer monomer *via* a chemical bond, and attapulgite serves as a crosslinking point in the resin, which is favorable for the formation of a porous three-dimensional network structure of the resin.^{21,24} The gelation reaction between the attapulgite nanoparticles and monomers changes the network structure of the polymer materials,^{13,30,36} further improving water absorption. The proportion was relatively low, or excess attapulgite only plays

a role in filling the pores, which results in a decrease in the water absorption ratio.^{16,32}

3.2. Effect of ultrasonic power on water absorbency

Two-way ANOVA showed that the WAR and SAR of the sand-fixing materials were significantly affected by ultrasonic treatment and the addition of attapulgite and their interaction (Table 2). The WAR was significantly different among the five ultrasonic treatments for all five sand-fixing materials with added attapulgite. Attapulgite addition significantly promoted the increasing WAR of the sand-fixing materials. The lowest WAR always appeared in ATP0 and ATP3 for all the ultrasonic treatments, which suggested that the lower dosages of attapulgite had no significant influence on the WAR of the SRA. Under 200 W of the ultrasonic treatment, ATP10 and ATP15 performed with larger WAR compared with other sand-fixing materials, and 300 W of the ultrasonic treatment could significantly improve the WAR of ATP10: the WAR of ATP10 reached a maximum value of 1168.55 g g^{-1} in distilled water (Table 3). The SAR was performed with almost coincident responses under the five ultrasonic treatments and different attapulgite additions. The SAR of the sand-fixing materials

Table 2 Analysis of variance for the effects of attapulgite addition and ultrasonic power, attapulgite addition and solution pH on water absorption rate, saline absorption rate and water retention capacity of the sand-fixing materials

Traits	Source of variation	df	F-value	P
Water absorption rate	Attapulgite	5	45.68	<0.001
	Ultrasonic power	4	11.24	<0.01
	Attapulgite \times ultrasonic power	20	235.49	<0.001
	Attapulgite	5	75.64	<0.001
	pH	4	6.27	<0.05
	Attapulgite \times pH	20	164.78	<0.001
Saline absorption rate	Attapulgite	5	36.54	<0.001
	Ultrasonic power	4	21.34	<0.001
	Attapulgite \times ultrasonic power	20	86.27	<0.001
	Attapulgite	5	11.25	<0.01
Water retention capacity	Ultrasonic power	4	8.26	<0.01
	Attapulgite \times ultrasonic power	20	65.24	<0.001

Table 3 Water absorption rate of the sand-fixing materials under different ultrasonic treatments at 60 min. Values with same lowercase letters were not significantly different among the ultrasonic treatments (column) and sand-fixing materials with addition of different contents of attapulgite (row) at $P < 0.05$ or according to Duncan's multiple comparison tests^a a* at 0.05 level, ** at 0.01 level, *** at 0.001 level for significant difference by ANOVA

Ultrasonic	ATP0	ATP3	ATP5	ATP8	ATP10	ATP15	F-value
CK	508.55E	606.99bD	849.89C	903.34B	989.77bA	849.89bC	14.16**
200 W	481.88D	621.01aC	1005.81B	1012.56B	1119.98bA	1005.81aB	65.37***
300 W	501.75D	586.93bC	962.98B	1092.77A	1168.55aA	971.23aB	36.57***
400 W	494.12D	558.73bD	900.04C	1014.10B	1107.71bA	904.34bC	24.38**
500 W	463.67D	563.85bC	856.61B	942.10A	996.45bA	843.67bB	12.39**
F-value	3.65	8.67*	4.36	4.52	9.41*	12.34*	

increased with the dosage of added attapulgite. A lower dosage (3%) of attapulgite had no significant influence on the SAR under all the ultrasonic treatments. ATP10 and ATP15 always showed a larger SAR compared to the other sand-fixing materials, and ATP10 performed with the largest SAR, reaching 212.60 g g^{-1} in saline solution (Table 4).

The results could be explained on the basis that when the power and reaction rate were low. The lower water absorbency of the superabsorbent composites could not be responded the reaction completely. With increasing ultrasonic power, the formation of free radicals would be easier. When the ultrasonic power increased to 300 W, the number of active radicals distinctly increased, leading to the growth of long chains in the grafted polymer and formation of a regular three-dimensional network, thereby improving the water absorption of the composite material. When the ultrasonic power is greater than 300 W, the water absorption of the composite material does not further improve (Tables 3 and 4). Excessive ultrasonic power may lead to self-crosslinking between the polymer and attapulgite nanoparticles, thereby enhancing the degree of cross-linking. During this process, a large number of free radicals may terminate the growth of grafting chains in the three-dimensional network, which may be another reason for the loss of water absorption by the composite material under conditions of higher ultrasonic power. In addition, high-power ultrasound treatment can easily cause liquid splashing, making the reaction difficult to control. Therefore, this study chose 300 W as the optimal ultrasound power.

3.3. Effect of solution pH on water absorbency

The sensitivity of the sand-fixing materials to pH value was explored by investigating the WAR for various pH values ranging from 5.0 to 9.0 in water. Two-way ANOVA showed that water absorbency showed significant differences among the five pH treatments of water for ATP3, ATP10 and ATP15. The WAR for all water with five pH values was performed with significant differences among the six sand-fixing materials. Attapulgite addition significantly enhanced the increase in the WAR of the sand-fixing materials. The lowest WAR always appeared in ATP0 and ATP3, showing that higher dosages of attapulgite had a significant enhancement effect on the WAR of the sand-fixing materials for water with various pH values. ATP10 always performed with the largest WAR compared to the other sand-fixing materials and arrived at a maximum value of 1114.46 g g^{-1} in water with pH 6 (Table 5). The water absorbency of the six sand-fixing materials increased in the pH range for water of 5–6 and decreases in the pH range of 7–9. According to previous reports, repulsive electrostatic interaction and hydrogen bonding have been recognized as the main reasons for water absorbency at various pH values of water.

Under acidic conditions, most carboxylate anions are protonated, which limits the electrostatic repulsion between atoms in the composite material, enhances the hydrogen bonding between polymer chains, and leads to a contraction of the three-dimensional network structure in the composite material, thereby reducing water absorption. As the external pH value increases ($5 < \text{pH} < 6$), the ionization level of grafted chains in the composite material increases, leading to

Table 4 Saline absorption rate of the sand-fixing materials under different ultrasonic treatments at 60 min. Values with the same lowercase letters were not significantly different among the ultrasonic treatments (column) and sand-fixing materials with addition of different contents of attapulgite (row) at $P < 0.05$ or according to Duncan's multiple comparison tests^a a* at 0.05 level, ** at 0.01 level, *** at 0.001 level for significant difference by ANOVA

Ultrasonic	ATP0	ATP3	ATP5	ATP8	ATP10	ATP15	F-value
CK	54.35C	76.1cB	83.03cA	81.53cA	83.34dA	81.47cA	16.54**
200 W	54.83C	85.93bB	184.79aA	194.18aA	209.45aA	206.36aA	46.58***
300 W	65.11C	98.53bB	194.56aA	198.23aA	212.60aA	200.19aA	35.46**
400 W	58.11C	113.85aB	151.66bA	166.43bA	171.33bA	162.83bA	13.68*
500 W	68.47C	93.15bB	134.01bAB	153.27bA	158.95cA	152.04bA	26.54**
F-value	4.29	8.54*	16.87**	11.34*	32.46**	28.64**	



Table 5 Water absorption rate of the sand-fixing materials for water in different pH at 60 min. Values with same lowercase letters were not significantly different among pH values of water (column) and sand-fixing materials with addition of different contents of attapulgite (row) at $P < 0.05$ or according to Duncan's multiple comparison tests^a

pH	ATP0	ATP3	ATP5	ATP8	ATP10	ATP15	F-value
5	427.3C	505.24aC	870.48B	914.82abA	966.64bA	938.26abA	45.68***
6	432.86D	527.22aC	908.84B	931.54aAB	1114.46aA	966.64aA	123.56***
7	439.26D	536.26aC	926.36B	957.64aB	1074.40aA	990.62aB	56.87***
8	465.12D	523.94aC	906.90B	937.06aB	1025.66aA	985.3aAB	231.45***
9	414.2D	435.16bC	846.08B	866.74bB	971.4bA	886.10bB	65.32***
F-value	3.48	6.87*	4.12	3.66	12.45*	8.54*	

^a * at 0.05 level, ** at 0.01 level, *** at 0.001 level for significant difference by ANOVA.

disruption of hydrogen bonding interactions, an increase in osmotic expansion pressure between the hydrophilic network structure and external solution, and an increase in electrostatic repulsion energy between polymer –COO functional groups. The three-dimensional network structure space of the composite sand-fixing material may expand and transform into neutrality, thereby enhancing water absorption. This behavior is very beneficial for the stability of superabsorbers in various agricultural water conservation applications and desert surfaces. However, in alkaline water (pH > 8), excess sodium cations shield the complexation of –COO functional groups through charge shielding, inhibiting effective anion repulsion and reducing the water absorption of the composite material.^{25,26} Repulsive electrostatic interaction and hydrogen bonding have been considered the main causes affecting the water absorption of the materials under various environmental conditions.³⁴ At higher pH, hydrogen bonding interactions are eliminated, electrostatic repulsion between anionic groups increases, and the polymer network structure of the composite material tends to have a higher expansion rate. Due to the charge shielding effect of counter ions (Na⁺), the swelling rate in alkaline solution decreases. In other hydrogel systems, the dependence of the swelling properties of similar composites on pH has also been reported.²⁵ As the concentration of salt solution increases, the swelling ability significantly decreases. This well-known phenomenon is usually attributed to the “shared shielding effect” of additional cations, which leads to a decrease in anion–anion electrostatic repulsion, leading to a decrease in osmotic pressure (ion pressure) difference between the hydrogel network structure and external solution.^{13,37}

3.4. Effect of attapulgite addition and ultrasonic power on water retention

WRC is an important indicator for the sand-fixing materials in view of practical applications. In this research, the sand-fixing materials prepared with different dosages of attapulgite under various ultrasonic treatments were evaluated with the WRC. It was remarkable that ATP8 and ATP10 under 200 W and 300 W of the ultrasonic treatment performed with an outstanding WRC compared to other SRA. The WRC of ATP10 was significantly higher than those of other sand-fixing materials, and no (ATP0) and lower addition of attapulgite (ATP3) always restrained the lowest WRC (Table 6). This could give a result where the water retention was improved upon the incorporation of attapulgite. Moreover, the swollen water in the composite materials can be divided into bound water, half-bound water, and free water. Compared with bound water and half-bound water, free water has higher transferability and is easily lost under ultrasonic treatment.^{27–29} Ultrasonic treatment can effectively improve the stability and water absorption of the composite materials.³⁰ Adding a certain amount of attapulgite to the composite material increases the number of hydrophilic functional groups, such as –COOH and –COOH, resulting in a higher percentage of bound and half-bound water in the composite superabsorbent than free water, which significantly enhances the water retention ability of the formed polymer.^{31–35} Higher ultrasonic power (400 W and 500 W) could cause liquid splashes. Therefore, ultrasonic power of 300 W was chosen as the optimum treatment. The WRC of all SRA was always performed with a downward trend over time, and ATP8 and ATP10

Table 6 Water retention capacity of the sand-fixing materials under the different ultrasonic treatments at 24 h. Values with same lowercase letters were not significantly different among the ultrasonic treatments (column) and among addition of different contents of attapulgite (row) at $P < 0.05$ or according to Duncan's multiple comparison tests^a

Ultrasonic	ATP0	ATP3	ATP5	ATP8	ATP10	ATP15	F-value
CK	11.83B	13.14bB	19.4b	17.48bA	20.56cA	18.81bA	5.66*
200 W	14.63C	25.96aB	27.55aB	36.45aA	40.87aA	29.70aAB	36.52***
300 W	15.66C	28.51aB	29.84aB	32.58aAB	40.08aA	28.78aB	29.64***
400 W	12.84C	20.04bB	19.3bB	22.56abB	30.38bA	17.45bB	30.26***
500 W	11.54C	16.14bBC	19.43bB	19.48bB	29.68bA	13.58cC	18.26**
F-value	3.61	19.58**	7.47**	28.66***	17.38**	9.68**	

^a * at 0.05 level, ** at 0.01 level, *** at 0.001 level for significant difference by ANOVA.



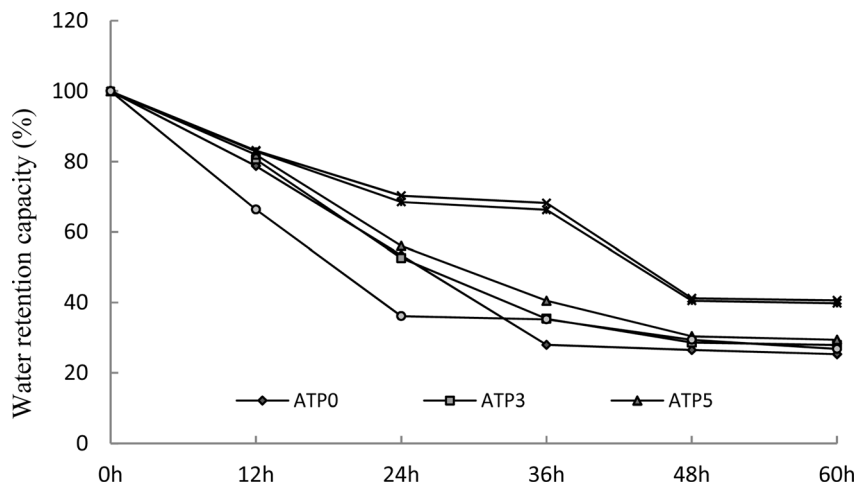


Fig. 4 Water retention capacity (WRC) of SRA.

presented better water retaining capacity (Fig. 4). Ultrasonication has a strong stirring effect on the liquid, where the localized high-temperature and high-pressure microenvironment that was formed *via* cavitation could lead to breaking and decomposition of polymer chains, and free radicals have an important effect on the solution polymerization.³⁰ However, the excessive cavitation that was generated by the excessive ultrasonic power would cause polymer chain breakage and hinder the formation of the three-dimensional network structure. In addition, high cavitation produced high temperatures and led to an increase in the reaction speed. The initiation of burst polymerization led to an increase in the number of oligomers, which increased the number of soluble components of the resin, namely, the number of short polymer chains.^{27,28}

4. Conclusions

The composite superabsorbent yielded the best absorption when the attapulgite content was 10% (mass fraction). Attapulgite clay has a significant effect on the water absorption rate and water retention when it is used as a framework structure matrix for preparing water absorbing materials. As the content of acid-modified attapulgite clay increased from 5% to 10%, the water absorption rate increased. When the content of attapulgite was too large, the increase in the number of crosslinking points led to an increase in the degree of crosslinking of the resin material and a decrease in the three-dimensional network structure. Excessive crosslinking agent leads to the formation of additional crosslinking points in the composite material, resulting in an additional adhesive network structure, thereby reducing the amount of space available for water to enter the composite material.

pH conditions had no significant effect on the water absorption of composite superabsorbents, and composite materials exhibit higher swelling ratios over a wider pH range. Due to the “charge shielding effect” of counter ions (Na^+), the swelling capacity in alkaline solutions of composite materials shows a decreasing trend.

The composite superabsorbent exhibited the highest absorption when the ultrasonic power was 200 W and 300 W. Attapulgite became more uniform in the monomer solution because of the ultrasonication. Ultrasonication facilitated the reaction of attapulgite and polymerized monomers and acted as an initiator. The combined effect caused the composites that were prepared under ultrasonic action to have higher water-absorption and brine-absorption rates than those that were prepared *via* conventional methods. High cavitation produced high temperatures and led to an increase in the reaction speed. The water absorption capacity of the polymer material increased with ultrasonic power.

Author contributions

Hanru Ren: visualization, methodology, resources, supervision, data processing. Ling Tao: conceptualization, investigation, data processing, formal analysis, visualization, supervision, funding acquisition. Jun Ren: methodology, resources, formal analysis, laboratory analyses. Xuechang Ren: conceptualization, investigation.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 31560234).

References

- 1 T. Chock, A. J. Antoninka, A. M. Faist, M. A. Bowker, J. Belnap and N. N. Barger, Responses of biological soil crusts to rehabilitation strategies, *J. Arid Environ.*, 2019, **163**, 77–85.



- 2 C. H. Park, X. R. Li, R. L. Jia and J. S. Hur, Combined application of cyanobacteria with soil fixing chemicals for rapid induction of biological soil crust formation, *Arid Land Res. Manage.*, 2017, **31**(1), 81–93.
- 3 X. H. Qi, M. Z. Liu, F. Zhang, Z. B. Chen, F. Zhang and L. Zhao, Preparation and properties of macroporous superabsorbent composite, *Polym. Adv. Technol.*, 2010, **21**(3), 196–204.
- 4 G. B. Marand, G. R. Mahdavinia and S. H. Ghafary, Swelling behavior of novel protein-based superabsorbent nanocomposite, *J. Appl. Polym. Sci.*, 2011, **120**, 1170–1179.
- 5 S. K. Patra and S. K. Swain, Swelling Study of Superabsorbent PAA-co-PAM/Clay nanohydrogel, *J. Appl. Polym. Sci.*, 2011, **120**, 1533–1538.
- 6 X. X. Su, Y. Y. Li, Z. J. Li, M. J. Li, Y. Zhao and M. D. Hao, Preparation and characterization of XG-g-P(AA-co-AM)/AC composite super absorbent resin, *Chem. Ind. Eng. Prog.*, 2011, **30**(7), 1556–1561.
- 7 X. N. Shi, W. Wang, Y. Kang and A. Wang, Enhanced swelling properties of a novel sodium alginate-based superabsorbent composites: NaAlg-g-poly (NaA-co-St)/PT, *J. Appl. Polym. Sci.*, 2012, **125**(3), 1822–1832.
- 8 W. B. Wang and A. Q. Wang, Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite, *Carbohydr. Polym.*, 2009, **77**(4), 891–897.
- 9 W. B. Wang and A. Q. Wang, Synthesis and swelling properties of guar gum-g-poly (sodium acrylate)/Na-montmorillonite superabsorbent nanocomposite, *J. Compos. Mater.*, 2009, **43**(23), 2805–2819.
- 10 A. Li, J. P. Zhang and A. Q. Wang, Utilization of starch and clay for the preparation of superabsorbent composite, *Bioresour. Technol.*, 2007, **98**, 327–332.
- 11 H. X. Yang, W. B. Wang and A. Q. Wang, A pH-sensitive biopolymer-based superabsorbent nanocomposite from sodium alginate and attapulgit: synthesis, characterization, and swelling behaviors, *J. Dispersion Sci. Technol.*, 2012, **33**, 1154–1162.
- 12 X. H. Qi, M. Z. Liu, F. Zhang and Z. B. Chen, Synthesis and properties of poly(sodium acrylate-co-2-acryloylamino-2-methyl-1-propanesulfonic acid)/Attapulgit as a salt-resistant superabsorbent composite, *Polym. Eng. Sci.*, 2009, **10**, 182–188.
- 13 J. F. Mukerabigwi, S. J. Lei, L. Fan, H. L. Wang, S. Y. Luo, X. Y. Ma, J. Qin, J. Q. Huang and Y. Cao, Eco-friendly nano-hybrid superabsorbent composite from hydroxyethyl cellulose and diatomite, *R. Soc. Chem.*, 2016, **6**, 31607–31618.
- 14 W. B. Wang, Y. Zheng and A. Q. Wang, Syntheses and properties of superabsorbent composites based on natural guar gum and attapulgit, *Polym. Adv. Technol.*, 2008, **19**(12), 1852–1859.
- 15 A. Li, Y. G. Zhao and A. Q. Wang, Study on superabsorbent composite. XII. effect of ion-exchanged attapulgit on water absorbency of poly(acrylic acid)/attapulgit superabsorbent composites, *J. Appl. Polym. Sci.*, 2007, **105**, 3476–3482.
- 16 A. Li, A. Q. Wang and J. M. Chen, Studies on poly(acrylic acid)/attapulgit superabsorbent composites. II. swelling behaviors of superabsorbent composites in saline solutions and hydrophilic solvent-water mixtures, *J. Appl. Polym. Sci.*, 2004, **94**(5), 1869–1876.
- 17 A. Li, A. Q. Wang and J. M. Chen, Studies on poly(acrylic acid)/attapulgit superabsorbent composite. I. synthesis and characterization, *J. Appl. Polym. Sci.*, 2004, **92**(4), 1596–1603.
- 18 S. K. Swain, B. B. Shur and S. K. Patra, Poly(acrylamide-co-vinyl alcohol)-superabsorbent materials reinforced by modified clay, *Polym. Compos.*, 2013, **10**, 1794–1800.
- 19 E. R. Kenawy, H. H. Elnaby and M. M. Azaam, Synthesis of superabsorbent composite based on chitosan-g-poly (acrylamide)/attapulgit, *Polym. Bull.*, 2024, **81**, 3527–3543.
- 20 Y. Liu, H. Chen, J. P. Zhang and A. Q. Wang, Effect of number of grindings of attapulgit on enhanced swelling properties of the superabsorbent nanocomposites, *J. Compos. Mater.*, 2012, **47**(8), 969–978.
- 21 X. N. Shi, W. B. Wang and A. Q. Wang, Effect of surfactant on porosity and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/attapulgit superabsorbent hydrogels, *Colloids Surf., B*, 2011, **88**, 279–286.
- 22 X. Y. Zhang, X. P. Wang, L. Li, S. S. Zhang and R. N. Wu, Preparation and swelling behaviors of a high temperature resistant superabsorbent using tetraallylammonium chloride as crosslinking agent, *React. Funct. Polym.*, 2015, **87**, 15–21.
- 23 L. Q. Peng, L. C. Zhou, Y. F. Li, F. Pan and S. D. Zhang, Synthesis and properties of waterborne polyurethane/attapulgit nanocomposites, *Compos. Sci. Technol.*, 2011, **71**, 1280–1285.
- 24 J. K. An, W. B. Wang and A. Q. Wang, Preparation and swelling behavior of a pH-responsive psyllium-g-poly(acrylic acid)/attapulgit superabsorbent nanocomposite, *Int. J. Polym. Mater.*, 2012, **61**, 906–918.
- 25 W. B. Wang and A. Q. Wang, Nanocomposite of carboxymethyl cellulose and attapulgit as a novel pH-sensitive superabsorbent: synthesis, characterization and properties, *Carbohydr. Polym.*, 2010, **82**, 83–91.
- 26 S. L. Shi, H. R. Zhang, C. Huang, X. Q. Lin and X. D. Chen, Purification of lignocellulose hydrolysate by org-attapulgit/(divinyl benzene-styrene-methyl acrylate) composite adsorbent, *BioResources*, 2016, **11**(4), 8664–8675.
- 27 J. H. Xu, T. Y. Gan, C. S. Peng and Z. Li, Synthesis and swelling behaviours of APT-gPAMPS superabsorbent composites by microwave irradiation, *Mater. Res. Innovations*, 2014, **18**, 377–381.
- 28 J. H. Xu, D. X. Tan, Z. Li, L. Y. Yan and W. J. Si, Characterization of attapulgit clay grafted AMPS/AM superabsorbent resin prepared by microwave irradiation, *Polym. Mater. Sci. Eng.*, 2012, **28**(12), 17–20.
- 29 G. F. Ma, F. T. Ran, E. K. Feng, Z. Zhang and Z. Q. Lei, Preparation and properties of an organic-inorganic composite superabsorbent based on attapulgit, *J. Compos. Mater.*, 2016, **50**(14), 1865–1874.
- 30 Z. Djamaa, R. Chebout, K. Bachari and D. Lerari, Microwave-assisted soft method for synthesis of poly (acrylic acid)/



- organo-clay composites: application as superabsorbent for phenol and Cr (VI), *ChemistrySelect*, 2023, **8**(42), e202302459.
- 31 J. F. Mukerabigwi, S. J. Lei, L. Fan, H. L. Wang, S. Y. Luo, X. Y. Ma, J. Qin, X. Y. Huang and Y. Cao, Eco-friendly nano-hybrid superabsorbent composite from hydroxyethyl cellulose and diatomite, *RSC Adv.*, 2016, **6**(38), 31607–31618.
 - 32 H. F. Li, L. R. Fan, L. R. Jing, J. Q. Song, M. S. Li and H. Q. Tian, Swelling behavior of palygorskite/poly(sodium acrylate) superabsorbent composites, *Acta Mater. Compositae Sin.*, 2009, **26**, 24–28.
 - 33 X. N. Shi, W. B. Wang and A. Q. Wang, Swelling behavior of guar gum-g-poly(sodium acrylate-co-styrene)/attapulgitic superabsorbent composites, *J. Macromol. Sci.*, 2011, **50**, 1847–1863.
 - 34 J. M. Zhang, H. Chen and A. Q. Wang, Study on superabsorbent composite. III. Swelling behaviors of polyacrylamide/attapulgitic composite based on acidified attapulgitic and organo-attapulgitic, *Eur. Polym. J.*, 2005, **41**(10), 2434–2442.
 - 35 W. B. Wang and A. Q. Wang, Synthesis and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/vermiculite superabsorbent composites, *J. Compos. Mater.*, 2011, **45**(21), 2189–2198.
 - 36 M. Sharma and A. Bajpai, Superabsorbent nanocomposite from sugarcane bagasse, chitin and clay: Synthesis, characterization and swelling behaviour, *Carbohydr. Polym.*, 2018, **193**, 281–288.
 - 37 Y. Liu, Y. F. Zhu, B. Mu, X. C. Wang and A. Q. Wang, Fenton-like redox-initiated synthesis of superabsorbent composites with excellent water retention and swelling properties based on green tea and oil shale semi-coke, *Eur. Polym. J.*, 2023, **182**, 111716.

