

Recovery of Ammonium onto Wheat Straw To Be Reused as a Slow-Release Fertilizer

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ABSTRACT: With the aim of improving fertilizer use efficiency and minimizing the negative impact of nitrogen pollution, a new multifunctional slow-release fertilizer was prepared by recovery of ammonium from aqueous solutions onto a superabsorbent composite. An eco-friendly superabsorbent composite based on wheat straw (WS) was synthesized and used as the carrier to control the release of nutrients. The adsorption studies with NH_4^+ indicated that the superabsorbent composite showed good affinity for NH_4^+ , with an adsorption capacity of 7.15 mmol g^{-1} when 20 wt % of WS was incorporated and that the adsorption system can reach equilibrium within 40 min. Afterward, the feasibility of reusing the composite as a multifunctional slow-release nitrogen fertilizer was investigated. The results showed that the product with good water-retention and slow-release capacities could regulate soil acidity and was economical and eco-friendly for application in agriculture and horticulture.

KEYWORDS: *slow-release fertilizer, superabsorbent, wheat straw, multifunctional*

■ INTRODUCTION

Agriculture must feed, clothe, and provide energy to a rapidly increasing world population while optimizing nutrient use from agronomic, economic, and environmental perspectives.¹ Fertilizer is the vital input material for the sustainable development of agriculture. Excessive applications of chemical fertilizers give rise to several agronomic and environmental problems.^{2,3} Nitrogen pollution in the hydrosphere recently has attracted attention to the eutrophication of lakes and rivers all over the world.^{4,5} NH_4^+ is an important species of nitrogen-containing compounds that acts as a nutrient for aquatic plants and algae.⁶ Hence, removing ammonium from wastewater is of great importance to control nitrogen pollution as well as the recovery of nitrogen from the wastewater and its reuse as fertilizer.^{7,8} Adsorption is a conventional but important separation process due to its high efficiency, easy handling, and availability of different adsorbents.^{9,10} Therefore, from a practical standpoint, an effective way to mitigate the aforementioned problem is to develop a slow-release fertilizer based on the recovery of ammonium from aqueous solutions by adsorption.

Superabsorbents are loosely cross-linked hydrophilic polymers with network structure, which have the ability to absorb and retain large amounts of aqueous fluids. Because of their superhydrophilicity and tailored functionality, the superabsorbents show several advantages over traditional adsorbents, namely, fast adsorption rate, high adsorption capacity, and ease of separation.¹¹ In addition, a large quantity of functional groups can be realized within the polymeric networks, making them exhibit some specific adsorption sites with affinity for the adsorbate.^{12,13} Furthermore, a test of superabsorbents for agricultural applications has shown encouraging results as they have been observed to help reduce irrigation water consumption, lower the death rate of plants, and improve fertilizer retention in soil.^{14,15} Therefore, the use of a superabsorbent for

the adsorption of ammonium and the preparation of slow-release fertilizer could impart the product's multifunctionality.

Wheat straw is available in abundance, is renewable, and is low in cost and already has been used widely for the removal of pollutants from wastewater.^{16–18} The main components of wheat straw are cellulose, hemicellulose, and lignin. There are various functional groups such as hydroxyl, carboxyl, phosphate, ether, and amino groups on these components.¹⁹ The existence of these functional groups is a good reason for wheat straw to be employed in the preparation of superabsorbent composites.^{20–22} Furthermore, when used as a fertilizer carrier, the recycling of crop residues could provide abundant nutrient elements²³ and organic matter for improving soil fertility.²⁴

In this study, we report the development of an eco-friendly slow-release fertilizer on the basis of adsorption of ammonium by the poly(acrylic acid-co-2-acryloylamino-2-methyl-1-propanesulfonic acid/wheat straw) (P(AA-co-AMPS)/WS) superabsorbent composite. The product was expected to improve fertilizer use efficiency and improve soil water content, regulate soil acidity and alkalinity level, and be beneficial to the ecosystem. Therefore, the objectives of this study were (1) to investigate the adsorption mechanism of ammonium onto the P(AA-co-AMPS)/WS superabsorbent composite and (2) to assess the feasibility of using the superabsorbent composite as the carrier material for the multifunctional slow-release fertilizer system.

■ MATERIALS AND METHODS

Materials. Wheat straw (WS, available from commercial sources) was smashed and dried at $105 \text{ }^\circ\text{C}$ in an oven for 8 h and then sieved to

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retain the 0.16–0.30 mm fraction. Acrylic acid (AA, chemically pure, Beijing Oriental Chemical Factory, Beijing, China) and 2-acryloylamino-2-methyl-1-propanesulfonic acid (AMPS, Shandong Linyi Viscochem Co., China) were used as received. *N,N'*-Methylene bisacrylamide (NNMBA, chemically pure, Shanghai Chemical Reagent Factory, Shanghai, China). Analytical grade ammonium chloride salt (NH_4Cl) and distilled water were used for the preparation of a stock NH_4^+ solution of 100 mmol L^{-1} . Ammonium solutions of different concentrations were prepared by diluting the NH_4Cl stock solution with distilled water. Other agents were all of analytical grade and were used directly as received.

Preparation and Characterization of P(AA-co-AMPS)/WS. A range of the superabsorbent composite polymers with different wheat straw content were prepared by the following procedure: 2.40 g of AA was placed in a flask and then neutralized with 4.5 mL of sodium hydroxide aqueous solution (6 M) in an ice bath. After that, 0.600 g of AMPS, 0.300 g of WS, 0.008 g of APS, 0.005 g of NNMBA, and 5.0 mL of distilled water were added successively to the partially neutralized AA solution under vigorous stirring. Finally, the flask equipped with a stirrer, thermometer, and nitrogen inlet tube was placed in a water bath, heated slowly to 70 °C, and maintained at this temperature for 3 h under nitrogen atmosphere. The resultant polymer was sheared, placed on a dish, and dried at 70 °C to a constant weight. The dried product was milled and screened.

The Fourier transform infrared (FTIR) spectra of the samples of WS, P(AA-co-AMPS), and P(AA-co-AMPS)/WS were obtained using a Nicolet NEXUS 670 FTIR spectrometer.^{3,7} All samples were prepared as potassium bromide tablets, and the scanning range was 500–4000 cm^{-1} .

The surface morphology of the superabsorbent composite was recorded using a JSM-5600LV scanning electron microscopy (SEM).^{7,20} Prior to the measurement, the dried samples were swollen in distilled water for 30 min and freeze-dried for 8 h with a Labconco freeze-dry system. Then, the samples were coated with a layer of gold and observed in the SEM.

Determination of Swelling Ratio of P(AA-co-AMPS)/WS. The procedures for determination of the swelling ratio were as follows: 0.2 g of superabsorbent composite particles (0.160–0.425 mm in diameter) were immersed into 100 mL of distilled water and allowed to swell at room temperature for 60 min. The swollen superabsorbent composite was filtered through an 80-mesh sieve to remove nonadsorbed water and weighed. The swelling ratio (SR) was calculated using the eq 1:

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

where M and M_0 denote the weight of the swollen and dried superabsorbents, respectively. All experiments were performed in triplicate.

Ammonium Adsorption onto P(AA-co-AMPS)/WS. Adsorption measurements were performed in a series of 100 mL conical flasks containing 0.1 g of superabsorbent composite particles (0.160–0.425 mm in diameter) and 50 mL of NH_4^+ solution. The mixtures were shaken in an incubator shaker (HNY-2102C) at 150 rpm for a given time, and then the superadsorbents were separated by filtration and dried at 30 °C to a constant weight. The nitrogen content (weight percent) of the superadsorbent was determined by elemental analysis performed on an Elementar Vario EL cube.^{3,23} Specifically, the samples underwent catalytic tube combustion in an oxygenated, high temperature atmosphere. The combustion gases were collected in a specific adsorption column. Concentrations of each component were determined by a thermal conductivity detector. The adsorption of the as-prepared superabsorbents for NH_4^+ was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e is the adsorption capacity of NH_4^+ onto the superabsorbent (mmol g^{-1}), C_0 and C_e are the concentrations of NH_4^+ in the initial

solution and in the aqueous phase after adsorption, respectively (mmol L^{-1}), V is the volume of the aqueous phase (L), and m is the weight of the dry superabsorbents (g).

To study the optimal adsorption conditions of the as-prepared superabsorbent composites, batch adsorption experiments were carried out at different contact times ranging from 0 to 150 min to illustrate the adsorption equilibrium at an initial NH_4^+ concentration of 50 mmol L^{-1} . Furthermore, to study the time dependence and investigate the adsorption mechanisms, the experimental data of NH_4^+ adsorption were fitted with pseudo-first-order (eq 3) and pseudo-second-order (eq 4) models:^{25,26}

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t are the amounts of the NH_4^+ ions adsorbed (mmol g^{-1}) at equilibrium and at time t (min), respectively; k_1 (min^{-1}) and k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$) are the rate constants of pseudo-first-order and pseudo-second-order kinetic equations of the adsorption, respectively.

For the adsorption isotherm studies, the initial NH_4^+ concentration was kept within 10–100 mmol L^{-1} with a contact time of 90 min at 15, 25, and 35 °C. The three important isotherm models were used to study the data. The linear equation of the Langmuir,²⁷ Freundlich,²⁸ and D-R²⁹ model isotherms can be expressed as eqs 5, 6, and 7, respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}} \quad (5)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (6)$$

$$\ln q_e = \ln q_m - K \varepsilon^2 \quad (7)$$

where C_e is the equilibrium concentration of NH_4^+ (mmol g^{-1}) in solution, q_e is the amount of ammonium ion adsorbed at equilibrium, q_{\max} (mmol g^{-1}) is the monolayer adsorption capacity of the superabsorbent, b (L mmol^{-1}) is the Langmuir constant, K_f (mmol g^{-1}) is the Freundlich constant, n (dimensionless) is indicator of adsorption intensity, q_m (mmol g^{-1}) is the theoretical saturation capacity, K is the constant related to the mean free energy of adsorption, and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$).

In addition, the effect of WS content on the adsorption of NH_4^+ onto the superabsorbent composite was investigated. The initial NH_4^+ concentration was kept within 70 mmol L^{-1} with a contact time of 90 min at 25 °C. All experiments were done in triplicate.

Preparation of Multifunctional Slow-Release Nitrogen Fertilizer (MSNF). To investigate the feasibility of using the P(AA-co-AMPS)/WS superabsorbent composite as the carrier material for a multifunctional slow-release fertilizer system, we prepared the quantity of adsorbed ammonium P(AA-co-AMPS)/WS. Specifically, 2 g of as-prepared superabsorbent composite particles (0.160–0.425 mm in diameter) were placed into a beaker with 1000 mL of 100 mmol L^{-1} ammonium aqueous solution at 25 °C for 8 h, and then filtered and dried at 30 °C. The dried adsorbed ammonium P(AA-co-AMPS)/WS particles (MSNF) with a nitrogen content of 11.2% were used to assess the slow-release behavior and the effect on the water-holding capacity and pH of soil.

Release Behavior of MSNF in Soil. To study the slow-release behavior of the MSNF in soil, the following experiments were carried out: 0.2 g of MSNF granules were embedded into a nonwoven bag. The bag was buried into a container with 200 g of dry soil (particle size smaller than 1 mm), 5 cm below the surface of soil. The proper amounts of untreated NH_4Cl was also carried out as the control test. Throughout the experiment, water-holding ratio of the soil was maintained at 20% by weighing and adding tap water if necessary periodically. The bags with MSNF granules were picked out after each incubated period (day 0.5, 1, 2, 4, 6, 8, and 10) and then dried at room temperature. Then, the fertilizer granules were removed from the bags

to be estimated for contents of nitrogen. The content of nitrogen was determined by elemental analysis. All experiments were performed in triplicate. The sierozem soil used in this study is a representative of Lanzhou, which lies in the northwest of China and is a semiarid region.³⁰

Measurement of the Water-Holding Capacity of Soil with MSNF. To study the effect of MSNF on the water-holding capacity of soil, the largest water-holding ratio of soil samples with different application rates (0.5, 1.0, and 1.5%) of MSNF were measured. A certain amount (0.5 g, 1.0 g, and 1.5 g) of MSNF was mixed with 100 g of dry soil (particle size smaller than 1 mm) and placed in a 4.5-cm-diameter PVC tube. The bottom of the tube was sealed with nonwoven fabric and weighed (marked W_1). The soil sample was drip-irrigated by tap water from the top of the tube until water seeped out from the bottom. When no water seeped at the bottom, the tube was weighed again (marked W_2). All experiments were performed in triplicate. The largest water-holding ratio (WH %) of soil was calculated from eq 8:

$$WH \% = \frac{(W_2 - W_1) \times 100}{100} \quad (8)$$

Effect of MSNF on the pH Value of Soil. Simulated soil solution samples with various pH values (4–10) were adjusted with 0.1 M HCl or NaOH aqueous. The MSNF (0.1 g) sample was immersed in the aforementioned 50 mL of soil solution with different pH values, and the flask was sealed for 60 min. After that, the swollen hydrogels were filtered, and the pH value of the filtrate was measured with a pH meter (pHS-3B, Shanghai Precision Scientific Instrument CO., Ltd., Shanghai, China).

Statistical Analysis. Statistical analysis of data was performed by one-way analysis of variance (ANOVA), assuming a confidence level of 95% ($p < 0.05$) for statistical significance.

RESULTS AND DISCUSSION

FTIR and SEM Characterization of the P(AA-co-AMPS)/WS Superabsorbents. In this study, P(AA-co-AMPS)WS can be formed in aqueous solution by a synchronous chemical graft of P(AA-co-AMPS) onto the wheat straw backbone and cross-linking reaction of NNMBA. FTIR spectra of WS, P(AA-co-AMPS), and P(AA-co-AMPS)/WS are shown in Figure 1.

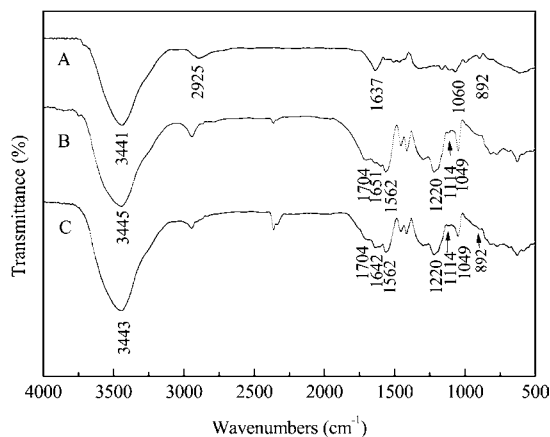


Figure 1. FTIR spectra of WS (A), P(AA-co-AMPS) (B), and P(AA-co-AMPS)/WS (C).

According to the spectrum of WS (Figure 1A), the absorptions were observed at 3441 cm^{-1} (hydroxyl stretching vibration), 1060 cm^{-1} and 892 cm^{-1} (β -1,4-glycosidic bond), and 2925 cm^{-1} (methyl and methylene), which were characteristic absorptions in the cellulose structure. The band at 1637 cm^{-1} was ascribed to C=O stretching from ketones, aldehydes, or

carboxylic groups of lignin.²¹ In the spectrum of P(AA-co-AMPS) (Figure 1B), the intense band at 3445 cm^{-1} should be attributed to the stretching of N–H and O–H bonds. The bands at 1704 cm^{-1} and 1642 cm^{-1} were ascribed to the stretching of C=O in –COOH and –COO[−] groups, respectively. The band at 1651 cm^{-1} was attributed to the stretching of C=O in the –CONH group. The adsorption bands at 1220 , 1114 , and 1049 cm^{-1} showed the appearance of –SO₃[−] group in AMPS. Comparing the FTIR spectrum of P(AA-co-AMPS)/WS (Figure 1C) with P(AA-co-AMPS), we observed additional peaks of WS (the peaks at 1637 and 1060 cm^{-1} corresponding to WS cannot be differentiated due to overlapping). On the basis of the analysis of FTIR, the conclusion can be drawn that a cross-linked copolymer of AA, AMPS, and WS was formed.

The SEM images of the P(AA-co-AMPS) and P(AA-co-AMPS)/WS superabsorbent composite containing 20 wt % of WS are depicted in Figure 2. It can be observed that the

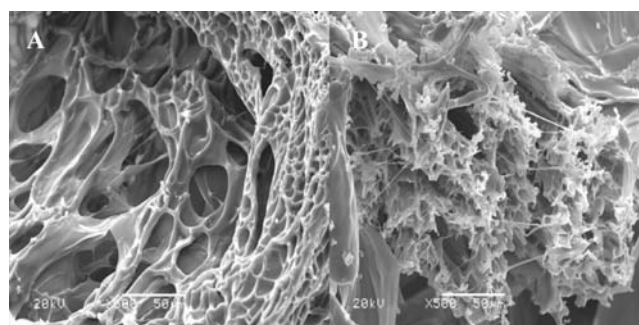


Figure 2. SEM images of P(AA-co-AMPS) (A) and P(AA-co-AMPS)/WS (B).

superabsorbents show the interconnected open channels, i.e., three-dimensional networks. One can speculate that NH₄⁺ ions are easily accessible to the active adsorption sites within the three-dimensional polymeric networks, and accordingly, the adsorption system would reach its equilibrium in a very short time.³¹

Effect of WS Content on Adsorption Capacity. The agricultural byproduct represents a potential alternative as an adsorbent because of its particular properties such as its chemical stability and high reactivity, resulting from the presence of reactive hydroxyl groups in polymer chains. The effects of WS content on the adsorption capacity were investigated, as shown in Figure 3. The adsorption capacity for NH₄⁺ increases with increasing WS content up to a maximum value of 10 wt % and then decreases with further increase in WS content. This property may be attributed to the higher SR of superabsorbent composite with 10 wt %. Higher swelling ratio can benefit from the higher adsorption capacity, and similar results have been reported by Kaşgöz et al.³² Compared with P(AA-co-AMPS), the introduction of 20 wt % WS into the polymer networks can afford comparable adsorption capacity for NH₄⁺ and lower application cost and thus is chosen to investigate its potential as a candidate for NH₄⁺ removal from an aqueous solution. Furthermore, the addition of WS is expected to (1) reduce the production cost as WS is abundant and inexpensive and (2) improve the biodegradability of the material for the utilization as fertilizer.

P(AA-co-AMPS)/WS Superabsorbents Adsorption Kinetic for NH₄⁺. Contact time is an important parameter

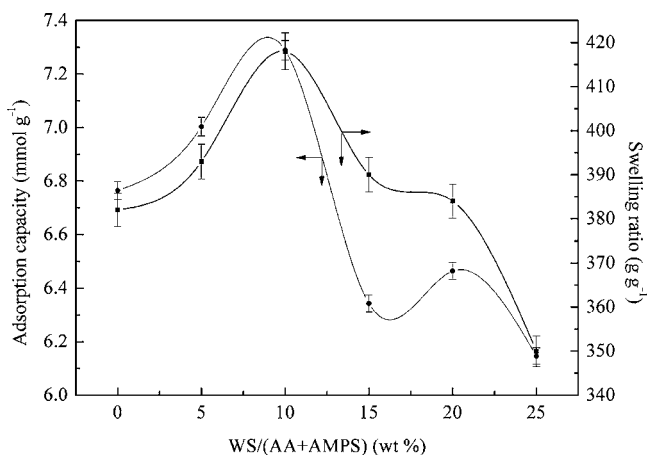


Figure 3. Effect of the WS content on the adsorption capacity of ammonium and swelling ratio of P(AA-co-AMPS)/WS (the arrows specify the left or right y-axis, which the curve follows).

because this factor can reflect the adsorption of an adsorbent for a given initial concentration of the adsorbate. The experimental results of NH_4^+ adsorption onto superabsorbents versus time at 25 °C is shown in Figure 4. As in Figure 4, q_e

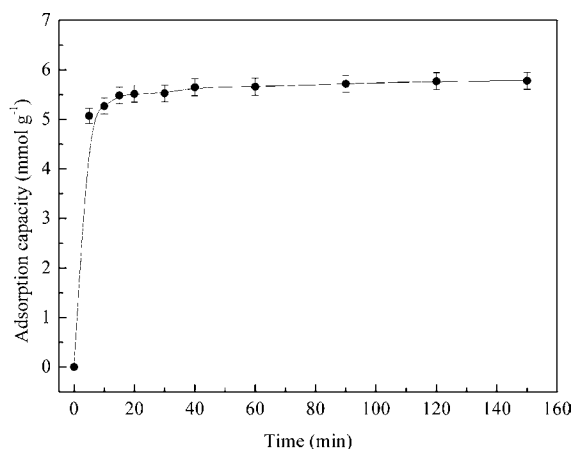


Figure 4. Effect of contact time on the adsorption capacity of ammonium onto the superabsorbent composite.

increases rapidly during the initial adsorption stage and then it continues to increase at a relatively slow speed with contact time and reaches the equilibrium point after 40 min. It was found that the NH_4^+ adsorption process is very fast, and >90% of the adsorption took place within the first 5 min.

The pseudo-first-order and pseudo-second-order models were tested for NH_4^+ adsorption onto the superabsorbent composite. The best-fit model was determined depending on the linear correlation coefficient R^2 . The fitted parameters of these kinetic models are listed in Table 1. The correlation coefficient of the pseudo-second-order model, which was close

to unity, was much higher than that of the pseudo-first-order model. In addition, the theoretical q_e value computed from the pseudo-second-order model was much closer to the experimental value q_{exp} given in Table 1. The information indicated that NH_4^+ adsorption onto the superabsorbent composite could be estimated more favorably by the pseudo-second-order model than the pseudo-first-order one.

Adsorption Isotherm Studies. The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption systems. Hence, the adsorption of NH_4^+ onto the composite at different temperatures was determined as a function of initial NH_4^+ concentration and demonstrated in Figure 5. It was observed

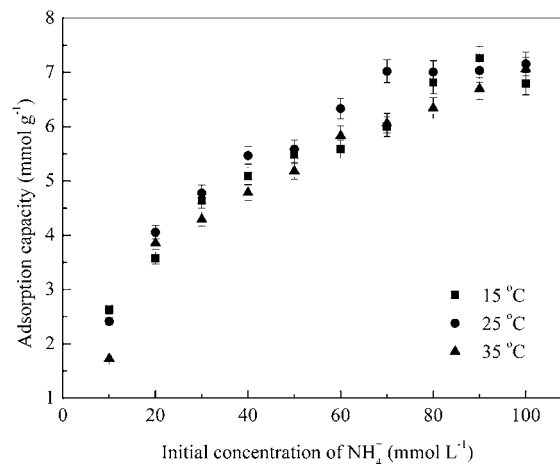


Figure 5. Adsorption isotherms of ammonium onto the superabsorbent composite at 15, 25, and 35 °C.

that the amount of adsorbed NH_4^+ increased gradually with increasing NH_4^+ concentration, as a result of the increased driving force of the concentration gradient.³³ The largest adsorption capacity is found to be 7.15 mmol per gram of adsorbent with the initial NH_4^+ concentration of 100 mmol L^{-1} at 25 °C.

For the systems considered, three important isotherms are selected in this study, which are, namely, the Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherms. The Langmuir model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The Freundlich model can be applied for nonideal sorption on heterogeneous surfaces and multilayer sorption. The D-R isothermal model is employed to determine the nature of the adsorption processes.

The parameters and correlation coefficients obtained from the plots of Langmuir and Freundlich for the adsorption of NH_4^+ onto the superabsorbent composite at different temperatures are summarized in Table 2. The fit of the data suggests that the Langmuir model gave closer fittings than Freundlich model, as is obvious from a comparison of the R^2 in Table 2. In addition, through the discussion for isotherm constants, it can

Table 1. Kinetic Parameters for the Adsorption of NH_4^+ onto Superabsorbent Composite^a

q_{exp} (mmol g^{-1})	pseudo-first-order model			pseudo-second-order model		
	q_{cal} (mmol g^{-1})	K_1 (min^{-1})	R^2	q_{cal} (mmol g^{-1})	K_2 ($\text{mmol g}^{-1} \text{min}^{-1}$)	R^2
5.78	0.993	0.0377	0.788	5.81	0.152	0.999

^aInitial concentration of NH_4^+ was 50 mmol L^{-1} , 25 °C.

Table 2. Isotherm Parameters for the Adsorption of NH_4^+ onto the Superabsorbent Composite at 15, 25, and 35 °C

T (°C)	Langmuir model				Freundlich model			D-R model	
	b (L mmol ⁻¹)	q_{max} (mmol g ⁻¹)	R^2	R_L	$1/n$	K_f	R^2	E_a (kJ mol ⁻¹)	R^2
15	0.0640	8.08	0.973	0.135	0.344	1.542	0.978	7.49	0.967
25	0.0693	8.39	0.993	0.126	0.374	1.465	0.955	7.39	0.983
35	0.0438	8.65	0.983	0.186	0.466	0.932	0.891	7.08	0.930

be predicted whether an adsorption system is favorable or unfavorable. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L ,³⁴ which is defined by

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

where C_0 is the highest initial ammonium concentration, and b is the Langmuir constant. The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).³⁴ As seen from Table 2, at all temperatures the R_L values were between 0 and 1.0, indicating that adsorption of NH_4^+ onto the wheat straw based superabsorbent composite is favorable.

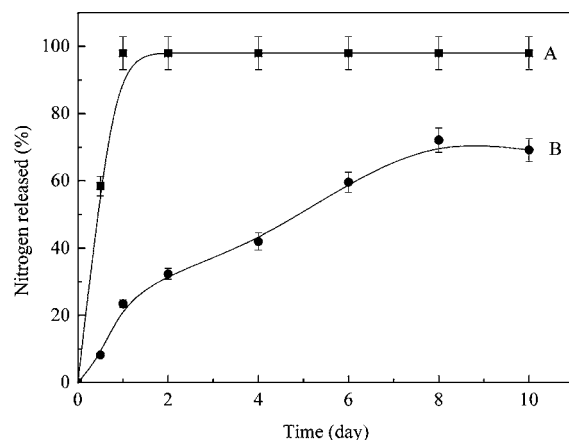
The D-R model could provide valuable information about adsorption mechanisms and physical or chemical processes from the mean energy of adsorption ($E_a = (2K)^{-1/2}$). The adsorption behavior is described as physical adsorption when E_a is between 1.0 and 8.0 kJ mol⁻¹, whereas it is considered as a chemical adsorption when E_a is more than 8.0 kJ mol⁻¹.^{29,35} Table 2 shows that the calculated E_a for NH_4^+ at all temperatures is lower than 8.0 kJ mol⁻¹, indicating that the adsorption behavior follows the physical adsorption process. It is known that there are three kinds of adsorption sites for the superabsorbent composite, i.e., $-\text{COO}^-$, $-\text{SO}_3^-$, and $-\text{CONH}$, which can be considered as the adsorption sites for electrostatic attraction and hydrogen bonding with NH_4^+ .

Thermodynamic parameters are the actual indicators for practical application of an adsorption process. According to the values of these parameters, which process will occur spontaneously can be determined. The values of free energy change (ΔG^0) for the sorption process were evaluated from Langmuir isotherms using the following eq 10:

$$\Delta G^0 = -RT \ln b \quad (10)$$

The estimated values of ΔG^0 for the adsorption of NH_4^+ onto superabsorbent composite were -9.96 , -10.49 , and -9.68 kJ mol⁻¹ at 15, 25, and 35 °C, respectively. The negative values of ΔG^0 imply the spontaneous nature of the adsorption process. Generally, the change in free energy for physisorption is between -20 and 0 kJ mol⁻¹, but chemisorption is a range of -80 to -400 kJ mol⁻¹.³⁵ The values of ΔG^0 obtained in this study were within the range of -20 to 0 kJ mol⁻¹, indicating that the physisorption was the dominating mechanism. The result of analysis for ΔG^0 confirms the mechanism of adsorption stated in the D-R isotherm model study.

Slow-Release Behavior of MSNF in Soil. The most important character of the MSNF was the slow-release property. Plots of the released percentage of nitrogen against time (days) are presented in Figure 6 for untreated NH_4Cl and MSNF in soil. It is well known that water-soluble compound fertilizer will be quickly dissolved in the soil solution after being added into soil and that the nutrient will be quickly exhausted. More than 98% of nitrogen in untreated NH_4Cl was released

**Figure 6.** Nitrogen release behaviors of untreated NH_4Cl (A) and MSNF (B).

within 24 h, as shown in Figure 6A. Compared with the untreated NH_4Cl , the release rate of nitrogen in the MSNF shown in Figure 6B decreased sharply. There, about 23.5, 42.0, and 69.2% of nitrogen was released after 1, 4, and 10 days, respectively. The slow-release property of MSNF is mainly due to the carrying material, P(AA-co-AMPS)/WS superabsorbent composite, which could be swollen slowly by soil solution and transformed into hydrogel after the MSNF was added into soil. There exists a dynamic exchange between the free water in the hydrogel and the water in soil.³⁶ The nutrients absorbed in the swollen hydrogel network would be diffused slowly from the network through the dynamic water exchange. Therefore, the as-prepared superabsorbent composite particles could be used as a carrier to control the release of the nutrient. In conclusion, the results of slow-release experiment demonstrated that the MSNF had the preferable slow-release characteristics and could improve plant nutrient use efficiency and minimize nutrient losses.

Water-Holding Capacity of Soil with MSNF. The presence of water in soil is essential to vegetation. Liquid water ensures the feeding of plants in nutritive elements. However, much farmland in the world is short of water in the dry season, in arid regions, and in desert regions. At the same time, most of the rainwater is lost in the rainy season, and the water resources cannot be used efficiently. Therefore, one method for effective utilization of the water resources involves the use of a superabsorbent that has the ability to absorb and retain large amounts of aqueous fluids.^{37–39}

Besides its slow-release property, another of the most important characteristics of the MSNF was the water-holding capacity. In this regard, the test of MSNF for the largest water-holding ratio of soil was carried out. For the soil samples with MSNF application rates of 0, 0.5, 1.0, and 1.5%, the largest water-holding ratios were 40.0, 77.5, 109.0, and 139.5%, respectively, as shown in Figure 7. We can conclude that the addition of MSNF to soil could improve the water-holding

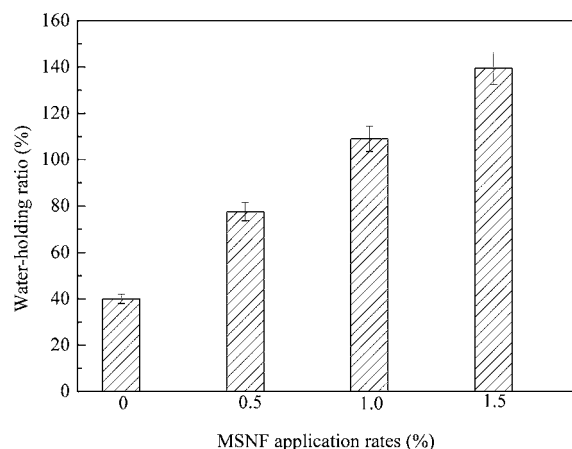


Figure 7. Water-holding capacity of soil with different application rates of MSNF.

capacity of the soil and the water content increase with an increasing amount of the MSNF in the soil. Therefore, the soil with the addition of MSNF could hold much more water during an irrigation period or rain than the soil without it and could efficiently reduce irrigation water consumption.

Effect of MSNF on Soil Acidity and Alkalinity. Soil pH is a value that refers to the acidity or alkalinity level in the soil. Soil pH affects all chemical, physical, and biological properties of soils.⁴⁰ In this study, the effect of MSNF on pH value of soil was investigated, and the results are shown in Table 3. As can

Table 3. pH Values of Soil Solutions by Treating with MSNF

	pH of soil solution						
initial value	4.0	5.0	6.0	7.0	8.0	9.0	10.0
after treating	6.8	6.8	6.7	6.8	6.8	6.9	7.1

be seen, the various pH values (4–10) of the simulated soil solution were adjusted to about 7.0 after treating with the MSNF. On the one hand, there were the exchange of counterions present in the polymer (Na^+ and NH_4^+) for acidic ions in soil solution, as observed by Guiwei et al.⁴¹ On the other hand, P(AA-co-AMPS)/WS superabsorbent polymers contain $-\text{COOH}$ and $-\text{SO}_3\text{H}$ groups, which can react with OH^- of the soil solution. The result means that the MSNF can buffer soil acidity or alkalinity so as to develop a more optimal pH for plant growth. Consequently, the soil environment became more favorable for plant growth, as P(AA-co-AMPS)/WS superabsorbents used in this study not only absorb water and increase water availability to crops but also adjust the pH value of the soil as a kind of soil amendment.

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ABBREVIATIONS USED

AA, acrylic acid; AMPS, 2-acryloylamino-2-methyl-1-propanesulfonic acid; APS, ammonium persulfate; b , Langmuir constant; C_0 , initial concentration of solution; C_e , concentration of solution after adsorption; FTIR, Fourier transform infrared; K , constant related to the mean free energy; k_1 , rate constant of pseudo-first-order; k_2 , rate constant of pseudo-second-order; K_f , Freundlich constant; MSNF, multifunctional slow-release nitrogen fertilizer; n , Freundlich constant; NNMBA, N,N' -methylene bisacrylamide; P(AA-co-AMPS), poly(acrylic acid-co-2-acryloylamino-2-methyl-1-propanesulfonic acid); P(AA-co-AMPS)/WS, poly(acrylic acid-co-2-acryloylamino-2-methyl-1-propanesulfonic acid)/wheat straw; q_{cal} , theoretical value of adsorption capacity; q_e , the amount of ammonium ion adsorbed at equilibrium; q_{exp} , experiment value of adsorption capacity; q_{max} , maximum adsorption value; q_t , the amount of ammonium ion adsorbed at time t ; r^2 , correlation coefficient; rpm, revolution per minute; SEM, scanning electron microscopy; SR, swelling ratio; WH, water-holding ratio; WS, wheat straw; ϵ , Polanyi potential

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