



# Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it

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## ARTICLE INFO

### Article history:

Received 1 December 2008

Received in revised form 5 December 2008

Accepted 10 December 2008

Available online 24 December 2008

### Keywords:

Wheat straw

Superabsorbent composite

Equilibrium water absorbency

Urea

## ABSTRACT

Wheat straw (WS) was used as raw material for synthesizing a novel wheat straw-g-poly(acrylic acid) (WS/PAA) superabsorbent composite by graft polymerization with wheat straw powder and acrylic acid in aqueous solution. The effect of wheat straw on water absorbency was discussed and the highest water absorbency was obtained when the amount of wheat straw in the feed was 20%. The superabsorbent composite was characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The results of FTIR spectra showed —OH of WS participated in graft polymerization with acrylic acid. The influences of pH, cations and anions on equilibrium water absorbency of WS/PAA were investigated. The superabsorbent composite was swollen in aqueous solution of urea to load urea, and the results showed urea concentration had no obvious effect on the swelling behaviors of WS/PAA. Furthermore, the release of urea from loaded WS/PAA was analyzed in water and in soil. Urea diffusion coefficient  $D$  was calculated.

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## 1. Introduction

Superabsorbents are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining possibly huge volumes of water in swollen state. 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, improve fertilizer retention in soil (Tomaszewska & Jarosiewicz, 2002). However, its applications in this field have met some problems because most of these superabsorbents are based on pure poly(sodium acrylate), and then they are too expensive, nonbiodegradable and not suitable for saline-containing water and soils. Recently, there have been many reports on introducing starch, cellulose and lignin, inorganic clays and chitosan into pure polymeric superabsorbents in order to improve swelling property, reduce production costs and ensure biodegradability (Farag & Al-Afaleq, 2002; Shogren, Willett, & Biswas, 2009; Zhang, Wang, & Wang, 2007). However, the researches on superabsorbent polymer based on crops residues are still few to see.

Till now, researches on utilization of crops residues, such as wheat straw, wheat straw and corn stem, have been focused on burying them back to improve the fertility of the soil, using it as the material of paper industry and producing protein feed, alcohol and methane by microbial fermentation (Bertrand, Prevot, &

Chabbert, 2009). However, in this study we provide a novel method for the management of wheat straw, i.e. the incorporation of it into superabsorbent polymer. The main components of wheat straw are cellulose and lignin, which had been introduced into superabsorbent polymer early. Here, wheat straw was used directly to synthesize superabsorbent composite with poly(acrylic acid).

Highly water-swellable polymers were developed for slow release of agrochemicals and nutrients in agricultural applications (Chatzoudis & Rigas, 1998; Shavit, Reiss, & Shaviv, 2003). The combination of superabsorbents and fertilizers may improve nutrition of plants, and mitigate at the same time the environmental impact from water-soluble fertilizers, reduce evaporation losses, lower frequency of irrigation (Chatzoudis & Valkanas, 1995). Loading of a hydrogel is done typically by two methods (Bajpai & Giri, 2002). In the first method, the compound to be loaded is added to the reaction mixture and polymerized in situ whereby the compound is entrapped within the gel matrix. In the second approach, the dry gel is allowed to swell in the compound solution and after the equilibrium swelling, the gel is dried and the device is obtained. There are some disadvantages to the first technique. For example, the entrapped compound may influence the polymerization process and the polymer network structure (Ward & Peppas, 2001); moreover, polymerization could have an adverse effect on the property of the entrapped compound. Urea, the entrapped compound in the present study, may change into biuret under the effect of polymerization heat, which is harmful to crops. Therefore, in the present study, the second method was adopted to load urea.

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On the basis of our previous work about superabsorbent composite (Liu, Liang, Zhan, Liu, & Niu, 2006, 2007), in this paper, a novel wheat straw-g-poly(acrylic acid) (WS/PAA) superabsorbent composite is synthesized by aqueous solution copolymerization. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) techniques are used to characterize it. The effect of wheat straw on water absorbency was discussed. The effects of pH, anions and cations and urea on swelling behaviors of WS/PAA are also investigated. The release of urea from loaded WS/PAA was studied in water and in soil.

## 2. Experimental

### 2.1. Materials

Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulphate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. *N,N*-Methylene-bisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corporation, Shanghai, China) was used as purchased. Wheat straw (WS) used in this study was agricultural residue of Xinxiang, China. The stalks crushed by disintegrator first and then ground to a 60 mesh particle size prior to use. All solutions were prepared with distilled water.

### 2.2. Preparation of wheat straw-g-poly(acrylic acid) superabsorbent composites

A series of superabsorbent composites with different amounts of wheat straw powder were prepared by the following procedure: a weight quantity of wheat straw powder and distilled water were put in a 250-mL four-necked flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line. The slurry was heated to 95 °C for 30 min under nitrogen atmosphere. The initiator APS (80 mg) was then added when the temperature reached 60–65 °C. After 15 min, 8 g of AA with 70% neutralization degree (neutralized with 25% ammonia in an ice bath) and crosslinker MBA (8 mg) mixture solution was added. The water bath was heated slowly to 70 °C and kept for 3 h. Then the resulting product was washed several times with distilled water and ethanol and then dried at 70 °C to a constant weight. The dried product was milled and screened. All samples used had a particle size in the range of 60–80 mesh.

### 2.3. Characterization

The IR spectra of the superabsorbent composite were recorded on a FTIR (Thermo Nicolet, NEXUS, TM) using KBr pellets. SEM studies were carried out on a JSM-5600LV SEM instrument (JEOL, Ltd.) after coating the sample with gold film using an acceleration voltage of 20 kV. TGA was recorded on a Netzsch STA-449C thermogravimetric analyzer, in the temperature range of 25–600 °C at a heating rate of 10 °C/min using dry nitrogen purge at a flow rate of 30 mL/min.

### 2.4. Measurement of equilibrium water absorbency

A weighted quantity of the superabsorbent composite was immersed in distilled water at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtered over a 100-mesh screen. The equilibrium water absorbency ( $Q_{eq}$ ) of superabsorbent composite was determined by weighing the swelled samples, and the  $Q_{eq}$  of the samples was calculated using the following equation:

$$Q_{eq} = (m_2 - m_1) / m_1 \quad (1)$$

where  $m_1$  and  $m_2$  are the weights of the dry sample and the water-swollen sample, respectively.  $Q_{eq}$  was calculated as grams of water per gram of sample.

The determination of water absorbency at various pH solutions was similar to that of above measurement. pH values of the external solution were adjusted via addition of 0.1 M HCl, 0.1 M NaOH.

Equilibrium water absorbency of the sample in various saline solutions (NaCl, KCl,  $\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2$ ,  $\text{FeCl}_3$ ) with different concentrations was tested according to the same procedure.

### 2.5. Loading of urea

The loading of urea was carried out by immersing pre-weighed dry gels into the aqueous solution of urea for 12 h. Thereafter, the swollen gels were dried at 40 °C for 3 days.

The loading percentage was calculated by the following Eq. (2):

$$\text{loading\%} = \frac{m_1 - m_0}{m_1} \times 100 \quad (2)$$

where  $m_0$  and  $m_1$  are the weights of unloaded and loaded dry gels.

### 2.6. Release of urea from WS/PAA in water

Loaded dry gel (0.5 g) was placed in beakers containing 1000 ml distilled water (release medium) without stirring, respectively. At various intervals, 2 ml solutions were drawn from the medium to follow the urea release. Urea was determined by a spectrophotometric method using *p*-demethylaminobenzaldehyde in a hydro alcohol medium with hydrochloric acid as reagent (Watt & Chrisp, 1954).

### 2.7. Release of urea from WS/PAA in soil

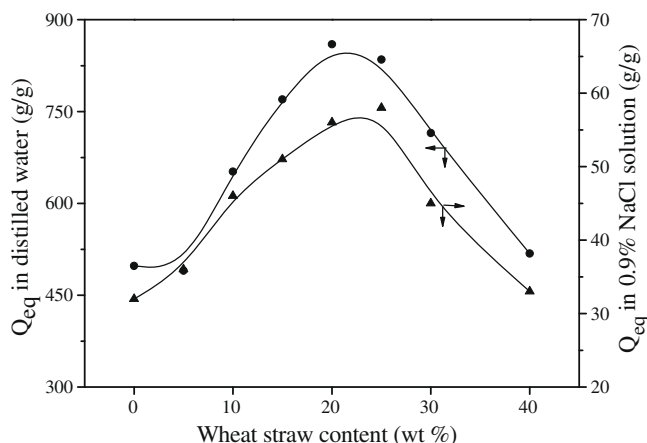
In order to demonstrate the release of urea from WS/PAA in agricultural field, release experiments in soil column were done. The soil used in this experiment was air-dried and sieved to less than 2 mm. PVC pipe of 45 mm internal diameter was used to hold soil. Loaded WS/PAA (2 g) was well mixed with 200 g dry sandy soil and placed in the PVC pipe. The bottom of the tube was sealed by nylon fabric. Water was added slowly by a perfusion tube (one drop every 10 s). We began to time when water seeped from the bottom of the pipe, i.e. water saturation. The leached water was collected, from which urea was estimated by the Kjeldahl method (AOAC, 1990). Control experiments, i.e. urea and urea/WS/PAA superabsorbent mixture (the amounts of urea were the same as that of loaded WS/PAA) were also carried out, respectively.

## 3. Results and discussion

### 3.1. Influence of wheat straw content on water absorbency

Water absorbency of the superabsorbent composites incorporated with different amounts of wheat straw in distilled water and in 0.92 wt% NaCl solution is shown in Fig. 1. It is clear that the amount of WS powder plays an important role in affecting equilibrium water absorbency of the WS/PAA superabsorbent composites. The water absorbency increases from 498 to 860 g/g as the amount of WS increases from 0 to 20 wt%, and further increasing the amount of WS decreases the water absorbency.  $Q_{eq}$  is 518 g/g even when 40 wt% WS is introduced, which significantly reduces production cost of the superabsorbent composite to be used in agriculture.

According to a previous study (Hua & Wang, 2009), sodium humate can react with AA to improve the polymeric network. In this



**Fig. 1.** Influence of wheat straw content on the  $Q_{eq}$  of WS/PAA superabsorbent composites.

study, a similar mechanism can be proposed, that is, the reactions between  $-\text{COO}^-$  groups and  $-\text{OH}$  groups on the surface of wheat straw powder can occur, and therefore enhances the water absorbency of the superabsorbent composite as the amount of WS increases from 0 to 20 wt%. The decreasing tendency of equilibrium water absorbency with further increasing WS content may be attributed to generation of more crosslink points in the polymeric network, inducing an increase in crosslink density of the composite, therefore, a decrease in the elasticity of the polymer. On the other hand, the water absorbency decreased with increasing WS content may be due to the that WS powder are partly physically filled in the WS/PAA network, the content of hydrophilic groups is lower and the water absorbency thus gradually decreases.

### 3.2. FTIR analysis of WS/PAA

The infrared spectra of wheat straw, PAA and WS/PAA superabsorbent composite containing 20 wt% wheat straw are shown in Fig. 2.

The main components of wheat straw are cellulose, hemicellulose and lignin. The raw wheat straw displayed the following bands: the band at  $3605\text{ cm}^{-1}$  is attributed to  $\text{O}-\text{H}$  stretching in hydroxyl functional groups. The bands at  $2950$  is ascribed to  $\gamma$   $\text{C}-\text{H}$  and  $\delta$   $\text{C}-\text{H}$  ( $\gamma$  = stretching and  $\delta$  = bending) absorption bands that may be present in methyl and methylene groups in cellulose. The relatively intense band at  $1745\text{ cm}^{-1}$  is ascribed to  $\text{C}=\text{O}$  stretching from ketones, aldehydes or carboxylic groups. The bands in the region  $1640\text{--}1430\text{ cm}^{-1}$  are ascribed to the skeletal  $\text{C}=\text{C}$  stretching vibrations in the aromatic rings bands. The band at  $1048\text{ cm}^{-1}$  is attributed to  $\text{C}-\text{O}$  stretching vibrations.

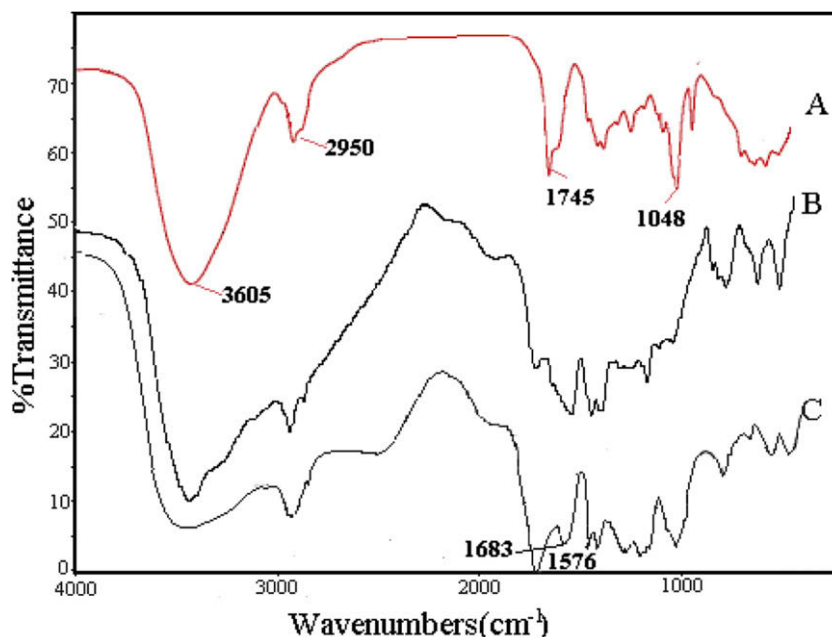
In the infrared spectrum of WS/PAA (the C line in Fig. 2), the absorption bands at  $1683\text{ cm}^{-1}$  is attributed to  $-\text{COOH}$  stretching, and  $1576\text{ cm}^{-1}$  is ascribed to asymmetric  $-\text{COO}^-$  stretching, which indicate the existence of PAA in the superabsorbent composite; the bands at  $1045\text{ cm}^{-1}$  ( $\text{C}-\text{O}$  stretching vibrations) and the bands near  $1450\text{ cm}^{-1}$  (the skeletal  $\text{C}=\text{C}$  stretching vibrations in the aromatic rings) indicate the existence of wheat straw in composite (some peaks corresponding to wheat straw can not be differentiated due to overlapping). Therefore, the resulting product was a composite based on PAA incorporating with WS.

### 3.3. Morphology of WS/PAA

The micrographs of crosslinked PAA, WS/PAA composite containing 20 wt% wheat straw are depicted in Fig. 3, respectively. It can be observed that crosslinked PAA (Fig. 3A) displays a smooth and tight surface. However, composites containing 20 wt% wheat straw (Fig. 3B) presents an undulant and coarse surface, which will facilitate the permeation of water into the polymeric network (Omidian, Hashemi, Sammes, & Meldrum, 1999).

### 3.4. TGA analysis of WS/PAA

TGA curves of PAA and WS/PAA superabsorbent composites are shown in Fig. 4. These samples show a similar loss at  $25\text{--}200^\circ\text{C}$ , indicating the loss of moisture present in these samples. The thermal decomposition process of PAA was divided into two steps, the first corresponding to decomposition of the carboxyl groups of



**Fig. 2.** FTIR spectra of wheat straw (A), PAA (B) and WS/PAA (C) superabsorbent composites containing 20 wt% wheat straw.

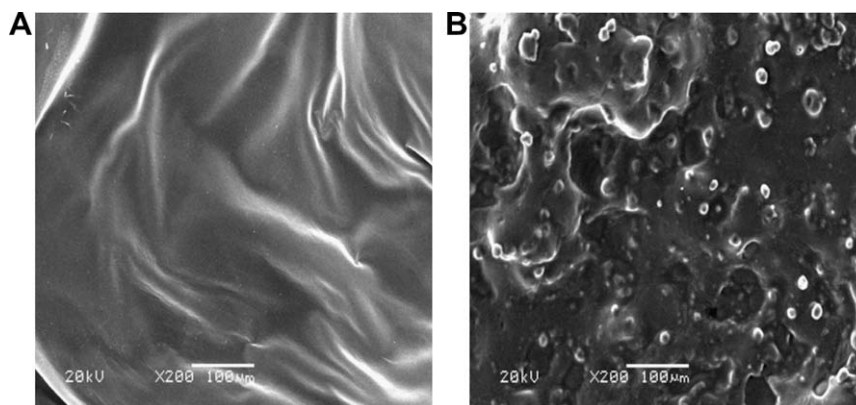


Fig. 3. Scanning electron micrographs for dried superabsorbents: (A) crosslinked PAA, (B) WS/PAA composites containing 20 wt% wheat straw.

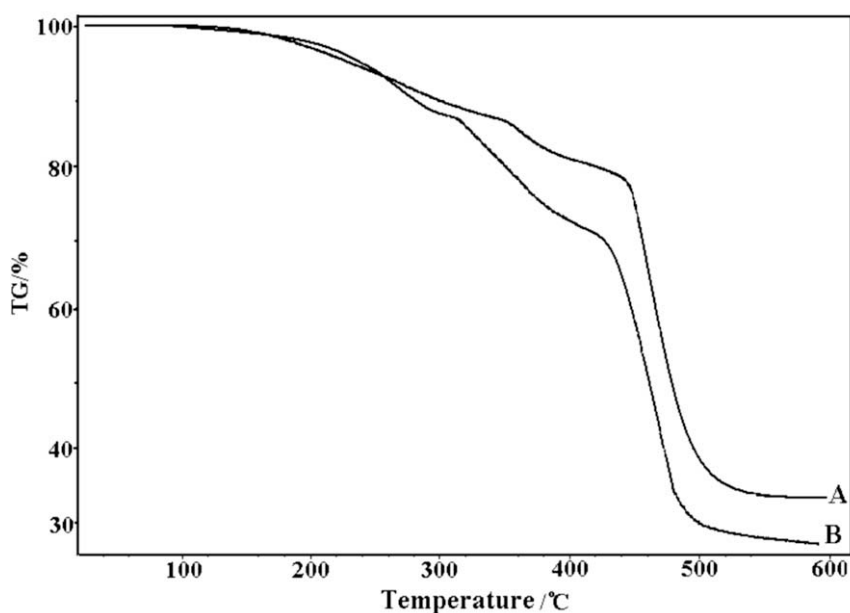


Fig. 4. TGA curves of PAA (A) and WS/PAA (B) superabsorbent composites at a heating rate of 10 °C/min.

PAA, and the second step is attributed to the breakage of the chains of PAA (Garay, Alava, & Rodriguez, 2000; Nicemol & Bini, 1998). The decomposition curve of WS/PAA superabsorbent composite could be divided into three steps. The first corresponded to the thermal degradation of WS; the second step was due to the decomposition of the carboxyl groups of the PAA chain; and the third step was associated with breakage of PAA chain. It also could be concluded from the experimental data: the total percentage weight loss of WS/PAA superabsorbent composite was higher than that of PAA; for the superabsorbent composite, the initial decomposition temperature and the temperature at the maximum decomposition rate of each step were obviously lower than those corresponding to PAA; and the temperature for 10% weight loss for superabsorbent composite were distinctly lower than that of PAA. All of these results demonstrate that the thermal stability of the WS/PAA superabsorbent composite was lower than that of PAA.

### 3.5. Influence of pH values on $Q_{eq}$ of WS/PAA

Partially neutralized poly(acrylic acid), which is the main component in WS/PAA superabsorbent composite, is a pH-sensitive

polymer, so the influence of pH on the  $Q_{eq}$  were also investigated at various pHs ranged from 3.0 to 12.0. Because absorbency of superabsorbent is strongly affected by ionic strength, no additional ions (through buffer solution) were added to medium for setting pH. Therefore, NaOH (pH 12.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

Experimentations showed that pH had no significantly influence on water absorbency at pH 5–10. The  $pK_a$  value of poly(acrylic acid) is known to be 4.8. Therefore, the carboxyl groups in PAA associate at pH < 4, thereby lowering the  $Q_{eq}$ . At higher pHs, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites ( $COO^-$ ) causes increasing in swelling ratios. At pH > 10, a screening effect (Keshava, Murali, Sreeramulu, & Mohana, 2006) of the counter ions, i.e.  $Na^+$ , shields the charge of the  $-COO^-$  groups and prevents an efficient repulsion. As a result, a remarkable decreasing in  $Q_{eq}$  is observed.

### 3.6. Influences of various cations and anions on $Q_{eq}$ of WS/PAA

The influences of various cations and anions on  $Q_{eq}$  were studied also. The  $Q_{eq}$  of WS/PAA superabsorbent composite in NaCl, KCl,

NH<sub>4</sub>Cl, MgCl<sub>2</sub>, FeCl<sub>3</sub> are given in Fig. 5, as a function of various concentrations.

It could be seen from Fig. 5,  $Q_{eq}$  of WS/PAA in all of the saline solutions were appreciably reduced comparing to the values measured in deionized water, and the  $Q_{eq}$  decreased with the increasing of the concentrations. This well-known phenomena, commonly observed in the swelling of ionic hydrogels, often result from a decreased osmotic pressure (ionic pressure) difference between the polymer network and the external solution. Donnan equilibrium theory is generally used to determine the osmotic pressure:

$$\pi_{ion} = RT \sum_i (C_i^g - C_i^s) \quad (3)$$

where  $C_i$  is the mobile ion concentration of species  $i$ , and super-scripts 'g' and 's' represent gel and solution phase, respectively. With the increasing of the chloride salt concentrations in swelling medium, the osmotic pressure difference between the gel networks and the external solution decreased, as a result, the water absorbency of WS/PAA decreased.

From Fig. 5, it also could be seen that  $Q_{eq}$  of WS/PAA decreased with the increasing charge of the cations (the order of  $Q_{eq}$  is  $K^+ > Mg^{2+} > Fe^{3+}$ ). This is because the divalent and trivalent ions could form complexes with carboxylate groups on WS/PAA (Zhao, Su, Fang, & Tan, 2005). This ionic crosslinking mainly occurs at surface of particles. It is found that WS/PAA hydrogels are rubbery and very hard when they swell in MgCl<sub>2</sub> and FeCl<sub>3</sub> solution. In contrast, the hydrogels swollen in univalent cation solutions exhibit lower strength. On the other hand, we found that the less the radius of the univalent cation, the more the water absorbency was. The radiiuses of Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> are 0.98, 1.33 and 1.42, respectively, and the order of  $Q_{eq}$  in chloride salt solutions is as follows: Na<sup>+</sup> > K<sup>+</sup> ≈ NH<sub>4</sub><sup>+</sup>.

Moreover, we found that the  $Q_{eq}$  of WS/PAA was irrelevant to the kind and valence of anion (KCl, K<sub>2</sub>SO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>) basically. A similar observation was recently reported for poly(aspartic acid) (Zhao et al., 2005).

### 3.7. Swelling of WS/PAA in aqueous solutions of urea

To load urea, WS/PAA superabsorbent composite was swollen in aqueous solutions of urea with the concentrations of 0, 0.5, 1 g/L. The equilibrium swelling degrees were 860, 855 and 862 g/g, respectively; and urea loading percentage were 0%, 28.3% and 51.9%, respectively. The results showed that  $Q_{eq}$  of WS/PAA in aqueous solutions of urea with different concentrations were al-

most equal, but urea loading percentage could be affected strongly by urea concentration. Moreover, no important differences in swelling rate were observed (the results are not given). That is to say, urea concentration has no obvious influences on the swelling process of WS/PAA superabsorbent composite. Similar phenomena and results had been reported by others (Karadağ, Üzümlü, Saraydin, & Güven, 2005).

The reason may be that urea is neutral molecule, which could not affect the electrostatic repulsion force of —COO<sup>−</sup> on polymer chain. Moreover, urea molecule has hydrophilic sites, such as —NH<sub>2</sub>. The addition of urea in water would not change the polymer–solvent interaction. Therefore, aqueous solutions of urea with different concentrations can hardly change the swelling process of WS/PAA composite.

The dependence of urea loading percentage on urea concentration could be interpreted as followings: when WS/PAA swelled in aqueous solutions of urea with higher concentration, more urea molecules entered into the polymer network. After drying, these urea molecules were left in the three-dimensional network, then the urea load percentage was high and vice versa. So, the urea loading percentage of WS/PAA could be modulated by the concentration of aqueous solutions of urea.

### 3.8. Release of urea from loaded WS/PAA in water and diffusion coefficient

Fig. 6 depicts the release profiles of urea from loaded WS/PAA (urea loading percentage: 28.3%) in distilled water. As expected, the release of urea shows a typical first-order release behaviors: an initially high release rate followed by a rapidly declining release rate.

The release of an active agent from hydrogel is classically assumed to take place by diffusion (Muhur & Blanshard, 1982). Diffusion coefficient thus appears as a key parameter. Urea diffusion coefficient has been achieved according to the following process.

A kinetic equation (Shavit, Shaviv, & Zaslavsky, 1995) with a cubic form had been derived to describe the diffusion control release behaviors of drug for a porous matrix ( $M_t/M_0 < 60\%$ ):

$$f_t = \frac{M_t}{M_0} = 3Kt^{1/2} - 3(Kt^{1/2})^2 + (Kt^{1/2})^3 \quad (4)$$

where  $f_t$  is the fraction of material released at time  $t$ , and  $K$  is the release rate constant.

This expression can be written in a linear form as:

$$(1 - f_t)^{1/3} = 1 - Kt^{1/2} \quad (5)$$

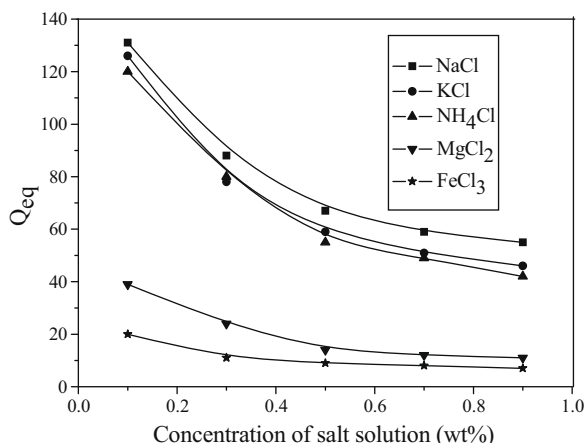


Fig. 5. Water absorbency of WS/PAA in NaCl, KCl, NH<sub>4</sub>Cl, MgCl<sub>2</sub> and FeCl<sub>3</sub> aqueous solutions with various salt concentration.

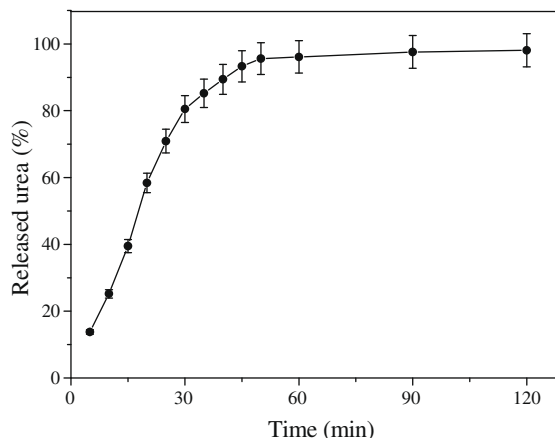


Fig. 6. The release of urea from loaded WS/PAA in distilled water.

By plotting the left-hand side of the above expression as a function of the square root of time, a linear plot with slope  $K$  is obtained.

The release rate constant  $K$  is defined as:

$$K = \left( \frac{1}{C_0} \times r_0 \right) [D(2C_0 - C_s)C_s]^{\frac{1}{2}} \quad (6)$$

where  $C_0$  is the weight of urea per unit volume of granular (it could be obtained for the urea loading percentage),  $C_s$  is the equilibrium solubility of the urea in the dissolution liquid,  $D$  is the diffusion coefficient of the urea in the swollen granular (including the effect of porosity and tortuosity) and  $r_0$  is the radius.

Calculation of diffusion coefficient  $D$  from the release rate  $K$  is possible:

$$D = \frac{(KC_0r_0)^2}{(2C_0 - C_s) \times C_s} \quad (7)$$

According to the above process, urea diffusion coefficient  $D$  is about  $6.2 \times 10^{-5} \text{ cm}^2/\text{s}$ . The value is bigger than the diffusion coefficient,  $10^{-6} \text{ cm}^2/\text{s}$ , reported in the literature (Shavit et al., 1995). The reason may be as followings: on a molecular level, solute diffusion through hydrogel depends on the porous structure of hydrogel, i.e. the mesh size of the pores in the hydrogel. The WS/PAA hydrogel obtained at the present experiment conditions were loosely crosslinked and the pore sizes in the hydrogel were big, then the obstruction effect exerted by the polymeric network was little. Therefore, the diffusion coefficient is high. Fig. 7 shows scanning electron microscopy picture of lyophilized WS/PAA. From Fig. 7, it could be seen that the pores in the WS/PAA hydrogel is big.

### 3.9. Release of urea from loaded WS/PAA in soil

Because there are many factors that could affect the release of urea from loaded WS/PAA in soil, such as the kind of soil, cation exchange capacity (CEC), water content, bulk density, urea concentration, gel collapse and so on, there must exist obvious differences for urea release from loaded WS/PAA between in distilled water and in soil. Therefore, we measured the urea release behaviors in soil.

Fig. 8 shows the urea release behaviors of loaded WS/PAA and untreated urea in soil. The urea release rate of untreated urea was very fast (as shown in Fig. 8A). While the urea release rate of loaded WS/PAA decreased obviously compared with that of urea, the result was in agreement with that of Smith (Smith & Harrison, 1991), as shown in Fig. 8B, the urea released 16.3%, 60.2% and

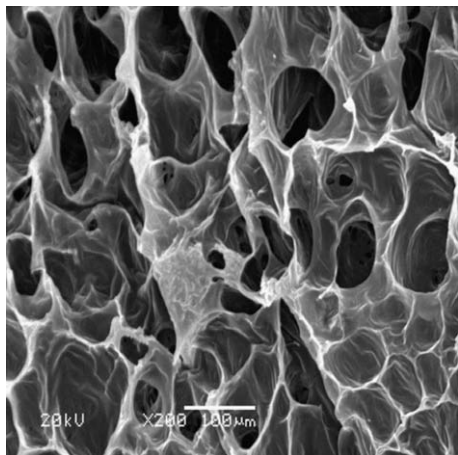


Fig. 7. Scanning electron microscopy pictures of lyophilized WS/PAA (swollen in distilled water, then frozen in liquid nitrogen and lyophilized).

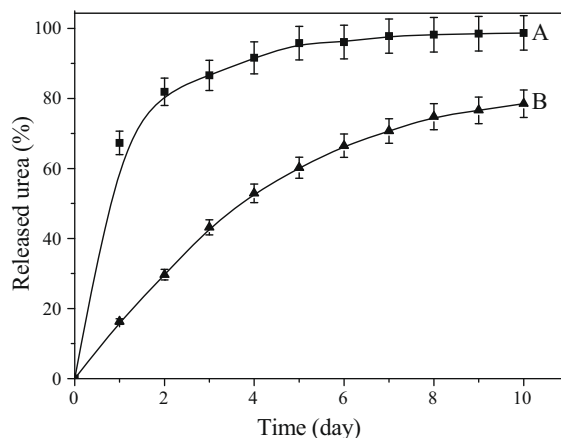


Fig. 8. The release of urea in soil. (A) untreated Urea; (B) loaded WS/PAA.

78.5% within 1, 5 and 10 days, respectively. The urea release characters of loaded WS/PAA in soil was similar to that in water, i.e. fast at beginning and slowed down gradually, except that the release rate was slow in soil.

It is well known that urea is easily dissolved in water, so it would quickly dissolve in the soil solution, and then release out of the soil by purge water, therefore, the release rate of untreated urea was very fast. However, for the loaded WS/PAA, the release of urea could be described by the following steps: (1) WS/PAA was slowly swollen by the water in soil and then transformed to hydrogel, and urea dissolved. (2) Urea could be released or desorbed slowly through the dynamic exchange of free water between soil solution and WS/PAA (David & Mark, 1994). (3) The released urea was purged out of the soil by water.

The reasons for the slower release rate in soil than in water may be due to the existing of many kinds of ions in soil solution, the swelling degree of WS/PAA is less in soil than that in distilled water, then the diffusion of urea in it would be difficult, which decrease the release rate of urea (Bajpai and Giri, 2002). Moreover, when the urea passed through the soil column, there are many-time absorbing and deabsorbing processes between urea molecule and soil granules, which also contribute to the slower urea release rate in soil.

## 4. Conclusion

A novel wheat straw-g-poly(acrylic acid) superabsorbent composite was synthesized by graft copolymerization reaction of wheat straw and AA in aqueous solution. The highest water absorbency was obtained when the amount of wheat straw in the feed was 20%. Water absorbency of WS/PAA is independent of pH between 4 and 10. The impact of cations on water absorbency of WS/PAA is relative to the valence and radius; the orders of water absorbency are  $\text{K}^+ > \text{Mg}^{2+} > \text{Fe}^{3+}$  and  $\text{Na}^+ < \text{K}^+ \approx \text{NH}_4^+$ , respectively. However, anions have no influences on water absorbency of WS/PAA. Concentration of aqueous solution of urea had no obvious effect on the swelling behaviors of WS/PAA. The urea loading percentage of WS/PAA could be modulated by the concentration of urea. The release of urea from WS/PAA in water was fast, the diffusion coefficient  $D$  is about  $6.2 \times 10^{-5} \text{ cm}^2/\text{s}$ , however, the release of urea from WS/PAA in soil was slow.

This paper showed a new method in utilizing crops residues such as wheat straw, corn and wheat stem, etc, in the production of superabsorbent material. The introduction of them into superabsorbent could significantly reduce the production cost and make the technique quite environmental friendly, which is crucial to superabsorbent for agricultural use.

## Acknowledgement

The authors gratefully acknowledge support of this research by the National Natural Science Foundation of China (No. 20877022).

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