

JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

2013 Volume 25 Supplement
www.jesc.ac.cn

The 5th International Symposium on Environmental Economy and Technology



Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

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Synthesis and characterization of agricultural controllable humic acid superabsorbent

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Abstract

Humic acid superabsorbent polymer (P(AA/AM-HA)) and superabsorbent polymer (P(AA/AM)) were synthesized by aqueous solution polymerization method using acrylic acid (AA), acrylamide (AM) and humic acid (HA) as raw material. The effects of N,N'-methylenebisacrylamide (MBA) crosslinking agent, potassium peroxydisulfate (KPS) initiator, reaction temperature, HA content, ratio of AA to AM, concentration of monomer and neutralization of AA on water absorption were investigated. Absorption and desorption ratios of nitrogen fertilizer and phosphate fertilizer were also investigated by determination of absorption and desorption ratio of NH_4^+ , PO_4^{3-} on P(AA/AM-HA) and P(AA/AM). The P(AA/AM-HA) and P(AA/AM) were characterized by Fourier translation infrared spectroscopy, biological photomicroscope and scanning electron microscopy (SEM). The optimal conditions obtained were as follows: the weight ratio of MBA to AA and AM was 0.003; the weight ratio of KPS to AA and AM was 0.008; the weight ratio of HA to AA was 0.1; the mole ratio of AM to AA is 0.1; the mole ratio of NaOH to AA is 0.9; the reaction temperature was 60°C. P(AA/AM-HA) synthesized under optimal conditions, has a good saline tolerance, its water absorbency in distilled water and 0.9 wt.% saline solution is 1180 g/g and 110 g/g, respectively. P(AA/AM-HA) achieves half saturation in 6.5 min. P(AA/AM-HA) is superior to P(AA/AM) on absorption of NH_4^+ , PO_4^{3-} . The SEM micrograph of P(AA/AM-HA) shows a fine alveolate structure. The biological optical microscope micrograph of P(AA/AM-HA) shows a network structure. Graft polymerization between P(AA/AM) and HA was demonstrated by infrared spectrum. The P(AA/AM-HA) superabsorbent has better absorbing ability of water and fertilizer, electrolytic tolerance and fewer cost than P(AA/AM) superabsorbent.

Key words: lignite humic acid; superabsorbent polymer; water absorbency; adsorption capacity; removal rate

Introduction

Low-carbon economy is not only an economic model based on low energy consumption, pollution and emission but also global revolution of production, lifestyles and values. Humic acid has many functions such as stimulating plant growth, enhancing the resistance of crops, improving soil structure and increasing soil retention of water and fertilizer. Taking advantage of the controlled release function, the usage of fertilizers and pesticides can be reduced (Cheng and Han, 2011). So humic acid is a nature low carbon material and worth further study.

As a hydrophilic polymer, superabsorbent has higher water absorbency than traditional water absorbing materials. While it was applied to soil, superabsorbent can reduce the irrigation frequency, prevent water losing, promote the formation of soil aggregate, improve soil structure, repeat water absorbing. Moreover, superabsorbent has a strong adsorption of NH_4^+ , PO_4^{3-} . When the soil fertilizer is sufficient, superabsorbent polymers absorb fertilizer. When

the plants need fertilizer from soil, nutrients absorbed was supplied for plants through exchange interaction. Therefore, superabsorbent polymer is one of the interesting directions in the field of low-carbon research (Huang et al., 2002; Li et al., 2002, 2004).

Ordinary superabsorbent polymers are very sensitive to electrolyte in solution. In this article, the humic acid superabsorbent polymer (P(AA/AM-HA)) was synthesized by aqueous solution polymerization with acrylic acid (AA), acrylamide (AM) and humic acid (HA) as raw material. The effects of N,N'-methylenebisacrylamide (MBA) crosslinking agent, potassium peroxydisulfate (KPS) initiator, reaction temperature, HA content, ratio of AA to AM, concentration of monomer and neutralization of AA on water absorption were investigated. Absorption and desorption ratios of nitrogen fertilizer and phosphate fertilizer were also investigated by comparison of P(AA/AM-HA) and P(AA/AM) to prepare superabsorbent for agriculture.

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1 Materials and methods

1.1 Instruments and materials

AA (chemical pure), AM (analytical grade), MBA (analytical grade), and KPS (analytical grade) were purchased from Shanghai Aladdin Reagents, China. Acrylic acid was distilled under reduced pressure before use. NaOH (analytical grade) and HA were extracted from lignite. The other reagents used were all analytical grade. All solutions were prepared using distilled water.

1.2 Preparation of coal based humate

Brown coal was ground into powder (80–100 mesh). A weighed brown coal 15 g and 200 mL NaOH (1.5 wt.%) solution were mixed and stirred for 1 hr in a three necked flask at 50°C. The mixture was separated by centrifugation. A appropriate (5 wt.%) HCl solution was added in the filtrate above. The sediment was as separated by centrifugation. Then sediment was washed with distilled water several times and dried in oven.

1.3 Preparation of P(AA/AM-HA)

A series of P(AA/AM-HA) superabsorbent composites with different amounts of AA, AM, MBA, KPS, HA and acrylic acid neutralization, were synthesized according to the following procedure. First, 1.1666 g of NaOH, 0.2589 g of AM, 0.0087 g of MBA and 5.0 mL distilled water was added in a beaker under ice water bath. The solution was stirred for 5 min. Then 2.625 g of AA and 0.2625 g of HA (neutralized with NaOH (1.5 wt.%) was added in the solution. At last, 0.0231 g KPS was dispersed in the mixed solution. The solution was transferred into a 250 mL three necked flask equipped with stirring rod and a nitrogen line. After being purged with nitrogen at 40°C for 20 min, the mixed solution was heated to 70°C gradually. The solution was stirred under nitrogen atmosphere to complete the polymerization reaction. The product was washed with distilled water to get rid of surplus monomer and KPS, and then dried in an oven until the weight of the product was constant.

1.4 Performance measurement of superabsorbent polymer

Water absorbency of resin was tested by natural filtering method. The resin was ground to powder in the range of 40–60 mesh. Then 0.15 g of resin and 500 mL of distilled water were mixed in a 1 L beaker. The left water was filtered by sieve after the resin was saturated in distilled water. The water absorbency of resin is calculated by following Eq. (1):

$$Q = (m_2 - m_1)/m_1 \quad (1)$$

where, m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively (Chen et al., 2009). Q was

calculated as grams of water per gram of sample. Finally, 250 mL of 0.9% saline was added into the above beaker. According to the above methods, the water absorbency in saline solution can be measured.

For the measurement of swelling rate, an accurate amount of samples (0.1000 g) were placed in a 500 mL beakers, then 300 mL of distilled water was poured into several beakers. The swollen resins were filtered by a sieve every 5 min, and the water absorbency of superabsorbent was measured by weighing the swollen resins and dry samples (Marcos, 2005) and was calculated by Eq. (1)

To determine the removal rate a weighed resin mixed with enough distilled water in a beaker. After saturation, the left water was filtered. The resin was weighed every 1 hr in the air (Zou, 2002).

NH_4^+ was measured according to Kjeldahl method (Ma, 2008). PO_4^{3-} was measured by vanadium molybdate yellow colorimetric method (Zhao et al., 2009).

1.5 Characterization

Fourier translation infrared spectra of samples were taken as KBr pellets using a FT-IR Spectrometer (WQF-200, Beijing Second Optical Instrument Factory, China). The micrographs of samples were taken using scanning electron microscopy ((SEM), Jnsl-5600VL, EJOL Japanese Electronics Joint-stock Company). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. The resin was also characterized by biological photomicroscope (213, Jiangsu Optical Instrument Factory, China).

2 Results and discussion

2.1 Effect of different factors on water absorbency of the superabsorbent

The effect of crosslinker content on water absorbency for superabsorbent is shown in **Fig. 1a**. Experimental condition are: NaOH/AA/AM = 0.8/1/0.125 (mole ratio), KPS/(AM+AA) = 0.7% (weight ratio), HA 2.625 g, AA/H₂O = 2.5/15 (volume ratio), temperature 60°C, with the protection of nitrogen.

The water absorbency in distilled water and 0.9 wt.% saline solution increases with increasing MBA content from 0.1×10^{-2} to 0.3×10^{-2} , but decreases with further increasing MBA content. The product with 0.3×10^{-2} MBA content achieves maximum water absorbency, 783 g/g and 110 g/g in distilled water and 0.9 wt.% NaCl solution, respectively. This may be attributed to the fact that with different MBA contents, MBA having bifunctional group creates different network with AA (Zhang et al., 2007). According to absorbing mechanism, superabsorbent polymer should possess three conditions (Cui et al., 2008): First, many hydrophilic groups; second, appropriate crosslinking degree; third, appropriate three-dimensional network structure which generates osmotic

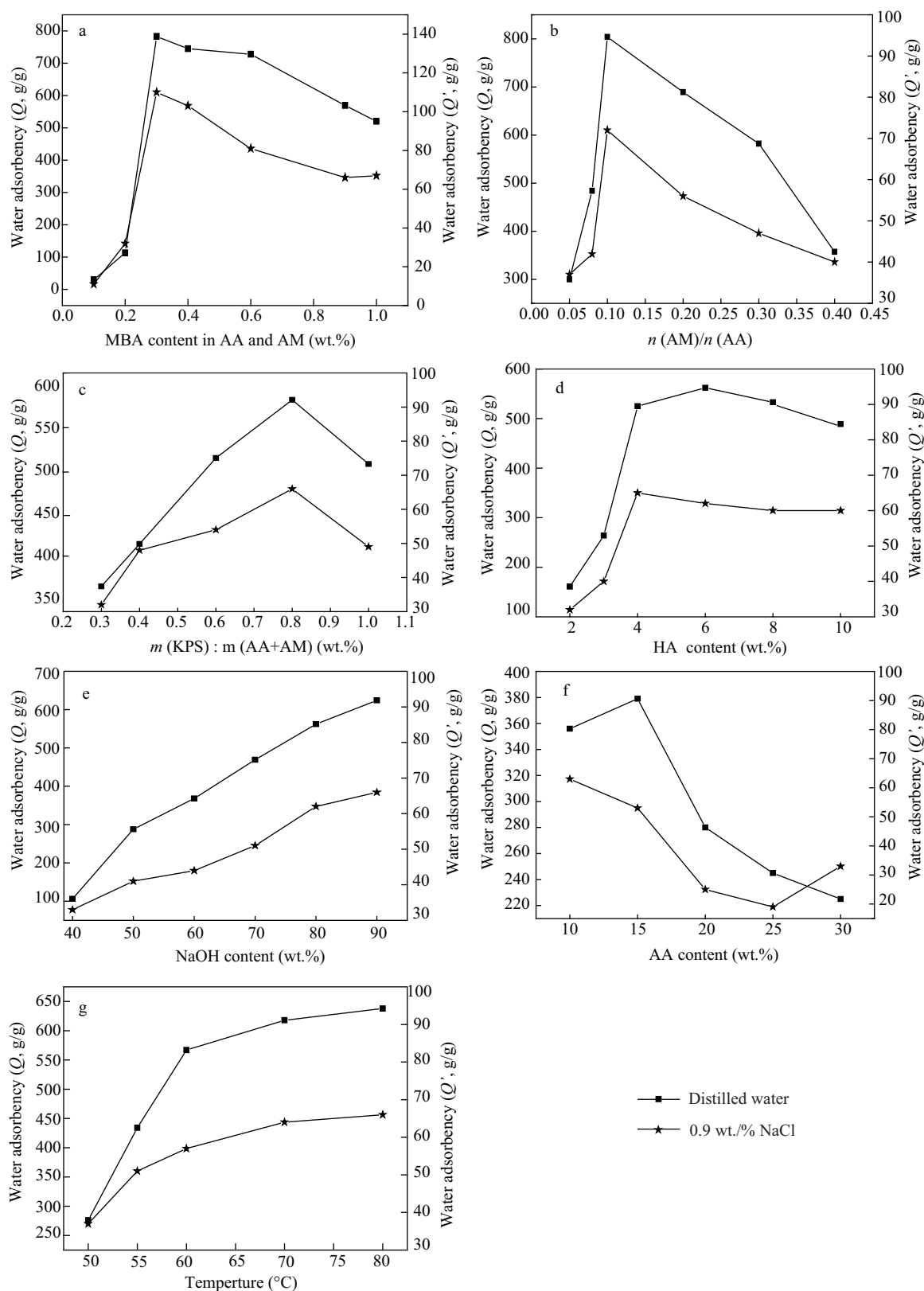


Fig. 1 Effect of MBA (a), AM (b), KPS (c), HA (d), NaOH (e), AA (f) content and temperature (g) on water absorbency of superabsorbent in distilled water (Q) and in 0.9 wt.% NaCl aqueous solution (Q').

pressure. When MBA content < 0.3%, water absorbency increases with increasing MBA content. This may be

attributed to the fact that MBA twines with P(AA/AM) chain, and creates network structure. When MBA content

> 0.3%, water absorbency decreases with increasing MBA content. This may be attributed to the fact that excessive crosslinking node limits network expansion (Chen et al., 2010). According to Flory theory (Flory, 1953) established in 1950s, water absorbency of the ionic resin greatly influenced by ionic strength (Eq. (2)). Therefore, water absorbency decreases in saline solution which has high ionic strength compared to distilled water.

$$Q^{\frac{2}{3}} \approx \frac{\overline{M}_c}{\rho_2} \left[\left(\frac{i}{2V_2S^{\frac{1}{2}}} \right)^2 + \frac{\frac{1}{2} - x}{V_1} \right] \quad (2)$$

where, Q (g/g) is water absorbency; i (C) is quantity of electric charge; S is ionic strength of solution; \overline{M}_c is molecular weight between two crosslinked points; ρ_2 (kg/L) is density of superabsorbent polymer; V_2 (L) is unit volume of superabsorbent polymer; V_1 (L/mole) is molar volume of solution; and x is parameter.

The effect of AM content on water absorbency for superabsorbent is shown in **Fig. 1b**. The conditions were as follows: NaOH/AA = 0.8/1 (mole ratio), KPS/AA = 0.7% (weight ratio), HA/AA = 1/10 (weight ratio), MBA/AA = 0.3% (weight ratio), AA = 2.5 mL, AA/H₂O = 2.5/15 (volume ratio), temperature 60°C, with the protection of nitrogen.

The water absorbency in distilled water and saline solution increase with increasing ratio of AM:AA from 5×10^{-2} to 10×10^{-2} mol/mol, but decrease with further increasing ratio of AM:AA. The product with ratio of 10% achieves maximum water absorbency, 804 g/g and 72 g/g in distilled water and 0.9 wt.% NaCl solution, respectively. It may be attributed to the fact that partly neutralize AA is ionic monomer, but AM is nonionic monomer. Polyacrylic acid superabsorbent polymer has higher water absorbency but lower absorbency rate. It's sensitive to electrolytical solution and has low water absorbency in 0.9 wt.% NaCl solution. Polyacrylamide resin has low water absorbency in distilled water but high water absorbency and absorbency rate in 0.9 wt.% NaCl solution (Cui, 2008). Thus carboxyl and amide groups are strongly hydrophilic functional groups. And synergistic effect between the carboxyl and amide groups greatly promotes water absorbency of P(AA/AM-HA) resin (Li and Wang, 2005). At the ratio of AA/AM = 0.1, resin makes maximum synergistic effect and water absorbency.

The effect of KPS content on water absorbency for superabsorbent is shown in **Fig. 1c**. The conditions were as follows: NaOH/AA = 0.8/1 (mole ratio), HA/AA = 1/10 (weight ratio), MBA/AA = 0.3% (weight ratio), AM/AA = 1/10 (mole ratio), AA = 2.5 mL, AA/H₂O = 2.5/15 (volume ratio), temperature 60°C, with the protection of nitrogen.

The water absorbency in distilled water and 0.9 wt.% saline increases with increasing initiator content from 0.3×10^{-2} to 0.8×10^{-2} , but decreases with further increasing

initiator content. The resin with 0.8% KPS content makes maximum water absorbency, 568.70 g/g and 65.50 g/g in distilled water and 0.9 wt.% NaCl solution, respectively. Initiator has a great effect on the reaction rate. When KPS content is not enough, it leads to shortage of active center. It also results in crosslinking degree insufficient, crosslinking nodes shortage, water absorbency decreasing and increasing solubility of resin. But when initiator content is excessive, the mixed solution is easy to initiate due to excessive active center. The repaid reaction rate and excessive reaction heat generated in a short time both result in implosion (Chen and Tan, 2006). So optimum KPS content is 0.8%, and resin has maximum water absorbency.

The effect of HA content on water absorbency for superabsorbent is shown in **Fig. 1d**. The conditions were as follows: NaOH/AA = 0.8/1 (mole ratio), MBA/AA = 0.3% (weight ratio), AM/AA = 1/10 (mole ratio), KPS/(AA+AM) = 0.8% (weight ratio), AA 2.5 mL, AA/H₂O = 2.5/15 (volume ratio), temperature 60°C, under the protection of nitrogen.

The water absorbency in distilled water and 0.9 wt.% saline increases with increase of humic acid content from 2×10^{-2} to 6×10^{-2} , and weakly decreases with further increase of HA content. When HA content is in range of 4–10 wt.%, the resin has similar water absorbency. There is little change between 6% and 10%. Thus 10% is the appropriate content. HA, complex organic macromolecules, contains free and bound phenolic –OH groups, quinone structures, nitrogen and oxygen as bridge units, –COOH and –NH₂ groups variously placed on aromatic ring (Sait et al., 2005). When the HA content < 6%, water absorbency increases with increasing HA content. This may be attributed to the increasing number of functional groups in the HA: free and bound phenolic –OH, –COOH, –NH₂, –SO₃, and quinonyl groups. These groups interact with acylamino and carboxyl groups and cause a collaborative absorbent effect to make water absorbency superior to that of isolated acylamino or carboxyl groups (Chu et al., 2010). On the other hand, the complex structures easily constituted by these functional groups of HA have strong chelation of ions in solution leading to the improvement of salt tolerance. When the HA content is above 10 wt.%, the decrease of water absorbency is attributed to the fact that the excess HA can't react with monomer and only acts as filler, which result in the decrease of the effective space to absorb more water (Liu et al., 2007).

The effect of acrylic acid neutralization on water absorbency of the superabsorbent is shown in **Fig. 1e**. The conditions were as follows: AA = 2.5 mL, MBA/AA = 0.3% (weight ratio), KPS/(AA+AM) = 0.8% (weight ratio), AM/AA = 1/10 (mole ratio), AA/H₂O = 2.5/15 (volume ratio), temperature 60°C, HA/AA = 1/10 (weight ratio), with the protection of nitrogen.

The water absorbency in distilled water and 0.9 wt.% saline solution increases with the increase of neutralization

degree. When the neutralization degree is 90%, the resin has maximum water absorbency, 623.69 g/g and 65.68 g/g in distilled water and 0.9 wt.% saline solution, respectively. The resin has low water absorbency with low neutralization degree. This may be attributed to high AA concentration and many active centers in mix solution, which lead to self polymerizing reaction and excessive crosslinked polymer (Gao et al., 2008). With increase of neutralization, resin has higher water absorbency. This may be attributed to that the reaction slows down and produces low crosslinked resin with increasing neutralization. The number of carboxylate groups which can easily be ionized into carboxyl ion and sodion compared with carboxyl ionization, increases with neutralization increasing. The increasing water absorbency may also be attributed to the increasing carboxyl ion availing for osmotic pressure enhancement and strengthen repulsion of polymeric chains availing for swelling of three dimensional network structure with increasing neutralization.

The effect of monomer concentration on water absorbency for superabsorbent is shown in **Fig. 1f**. The conditions were as follows: NaOH/AA = 0.8/1 (mole ratio), AA = 2.5 mL, MBA/AA = 0.3% (weight ratio), AM/AA = 1/10 (mole ratio), KPS/(AA+AM) = 0.8% (weight ratio), temperature 60°C, HA/AA = 1/10 (weight ratio), with the protection of nitrogen.

As can be seen, the resin has maximum water absorbency at 15% monomer concentration. When monomer concentration is larger than 15%, water absorbency decreases with the increase of monomer concentration. This may be attributed to the fact that high crosslinking degree results in water absorbency decreasing. When monomer concentration is less than 10%, there are excessive soluble materials.

The effect of temperature on water absorbency for superabsorbent is shown in **Fig. 1g**. The conditions were as follows: NaOH/AA = 0.9/1 (mole ratio), MBA/AA = 0.3% (weight ratio), AM/AA = 1/10 (mole ratio), KPS/(AA+AM) = 0.8% (weight ratio), HA/AA = 1/10 (weight ratio), AA 2.5 mL, AA/H₂O = 2.5/15 (volume

ratio), with the protection of nitrogen.

The water absorbency in distilled water and 0.9 wt.% saline increases with increasing temperature from 50 to 70°C, but slowly increases with further increase of the temperature. When the temperature is 70°C, the resin has water absorbency 618 g/g and 65 g/g in distilled water and 0.9 wt.% saline solution, respectively. KPS, as a thermal initiator should be heated to a certain temperature to produce radicals and initiate reaction. When temperature is less than 70°C, the water absorbency increased with the increase of the temperature. This may be attributed to the fact that there are more radicals produced to enhance reaction rate and grafting efficiency leading to increasing of crosslinking nodes and water absorbency. When temperature is larger than 70°C, the water absorbency decreased with the increase of the temperature. This may be attributed to the fact that with rising of reaction rate and crosslinking density there are more reactions of chain transfer and chain termination leading to the decrease of chain length and water absorbency (Wu et al., 2012). So the appropriate temperature is 60–70°C.

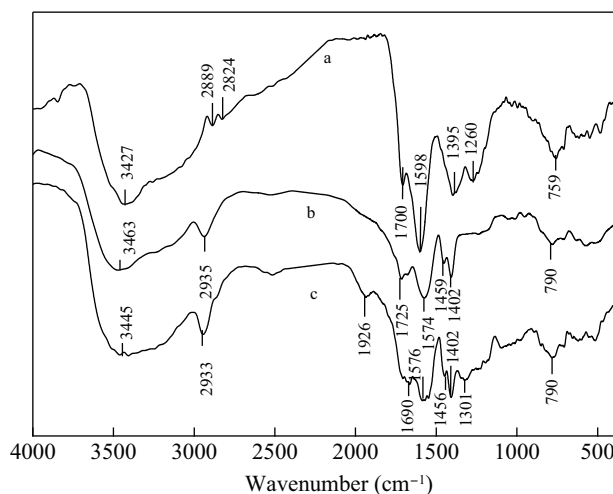


Fig. 3 Infrared spectrum of HA (line a), p(AA/AM) (line b) and P(AA/AM-HA) (line c).

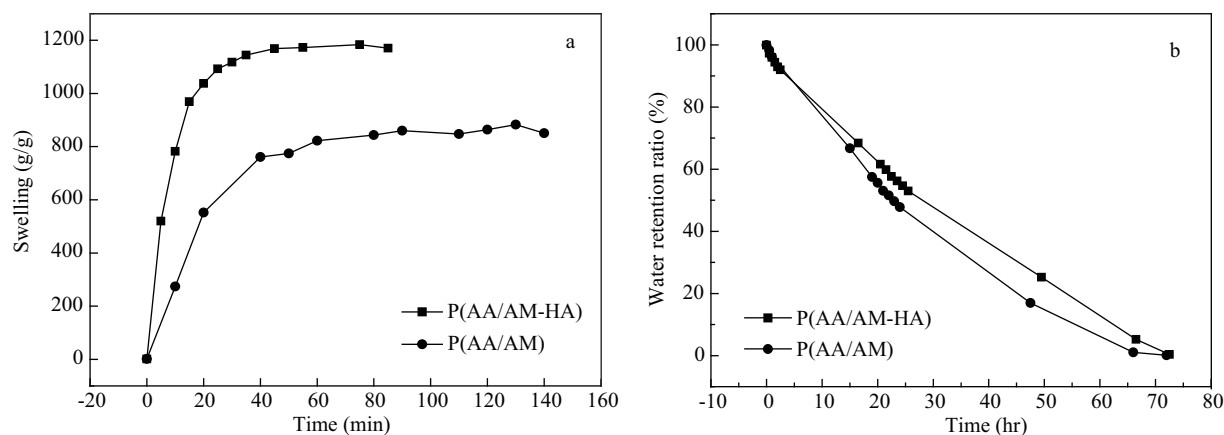


Fig. 2 Swelling (a) or releasing water ratio (b) of P(AA/AM-HA) and P(AA/AM).

2.2 Characterization of superabsorbent polymer

2.2.1 Swelling rate and releasing rate

The swelling rate of superabsorbent is investigated and shown in **Fig. 2a**. P(AA/AM) was prepared under the same condition of P(AA/AM-HA) without humic acid (the same below). It can be seen, the saturated water absorbency of P(AA/AM-HA) is much more than that of P(AA/AM). This may be attributed to the fact that HA functional groups with acylamino and carboxyl functional groups of resin interacts with each other and causes a collaborative absorbent effect to make P(AA/AM-HA) water absorbency superior to that of P(AA/AM). P(AA/AM-HA) was saturated in 30 min, but P(AA/AM) was saturated in 40 min. This may be attributed to the fact that resin mixed with HA generates alkyl-aryl-ester structure with high hydrophobicity, which accelerates speed of water molecules permeating into resin and drops possibility of pasting phenomenon in beginning of absorbing (Cui et al., 2008). The releasing rate of superabsorbent is investigated and shown in **Fig. 2b**. It can be seen, the releasing rate of P(AA/AM-HA) is slower than that of P(AA/AM). According to swelling and releasing rate of superabsorbent, P(AA/AM-HA) is more suitable for agriculture application.

2.2.2 Microstructure of superabsorbent polymer

The IR spectra of HA, P(AA/AM) and P(AA/AM-HA) are shown in **Fig. 3**. The strong absorption bands between $3500\text{--}3300\text{ cm}^{-1}$ are ascribed to hydrogen bond --OH in line a. A series absorption bands of HA at 1700 , 1598 , 1395 and 1260 cm^{-1} are ascribed to C=O stretching, aromatic C=C , --OH or phenolic hydroxyl C--O and sulfo group, which shows the existence of --COOH , phenolic hydroxyl and sulfo group. The strong absorption band between $3500\text{--}3300\text{ cm}^{-1}$ ascribed to hydrogen bond --OH and --NH_2 in line b and c. From line b, It can be seen that the absorption bands at 2935 , 1725 , 1459 and 1402 cm^{-1} are ascribed to C--H stretching, carboxyl C=O , $\text{--CH}_2\text{--}$ bending and C--N stretching, respectively. As it can be seen in line c, the absorption bands at 2933 , 1680 , 1576 , 1456 and 1402 cm^{-1} are ascribed to C--H stretching, carboxyl

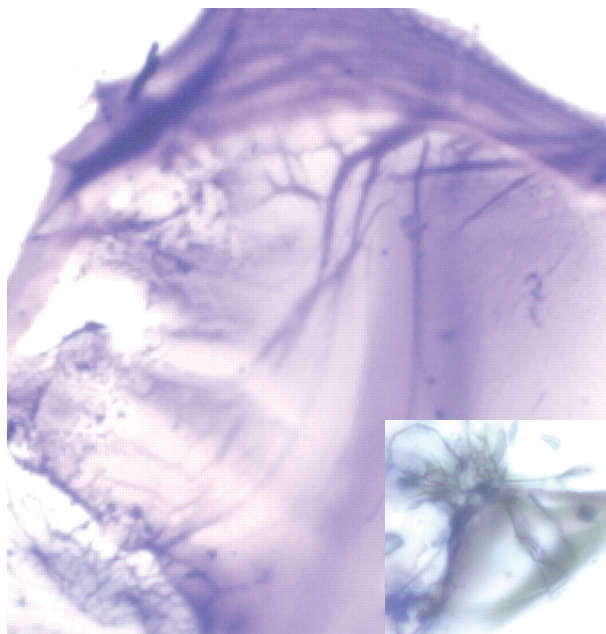


Fig. 5 Biological optical microscope photo of P(AA/AM-HA).

C=O , aromatic C=C , $\text{--CH}_2\text{--}$ bending and C--N stretching, respectively. The absorption band at 1301 cm^{-1} ascribed to an alkyl-aryl-ether indicates graft polymerization between P(AA/AM) and HA.

The surface morphologies of P(AA/AM-HA) and P(AA/AM) are shown in **Fig. 4**. P(AA/AM-HA) displayed a alveolate structure has more uniform porous structures and better loosened network than P(AA/AM). It also provides evidence of graft polymerization between P(AA/AM) and HA

The surface morphologies of P(AA/AM-HA) superabsorbent polymer are shown in **Fig. 5** with biological optical microscope when the resins were saturated with water. As it can be seen, the resin saturated with distilled water presents network structure and lamellar structure. These special structures have property of capillary absorption and water absorbing capacity.

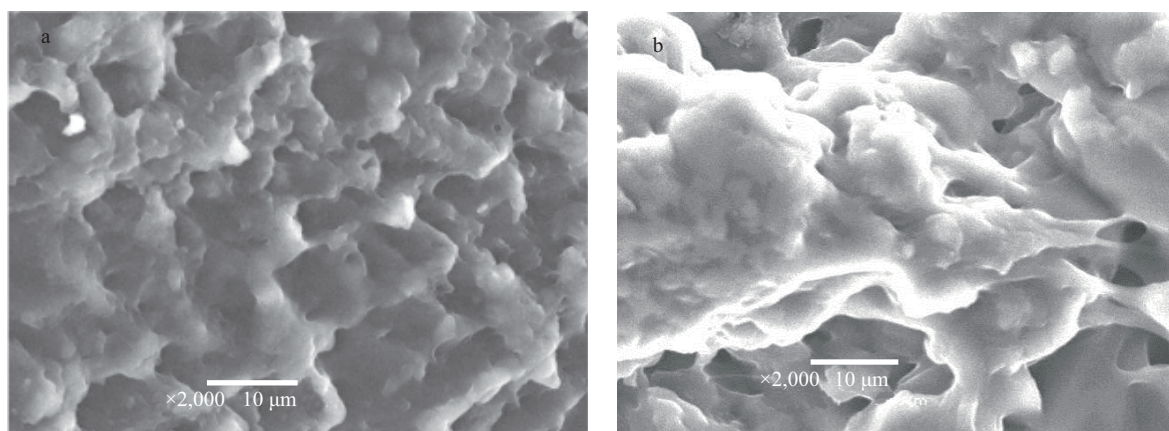


Fig. 4 SEM photos of P(AA/AM-HA) (a) and P(AA/AM) (b).

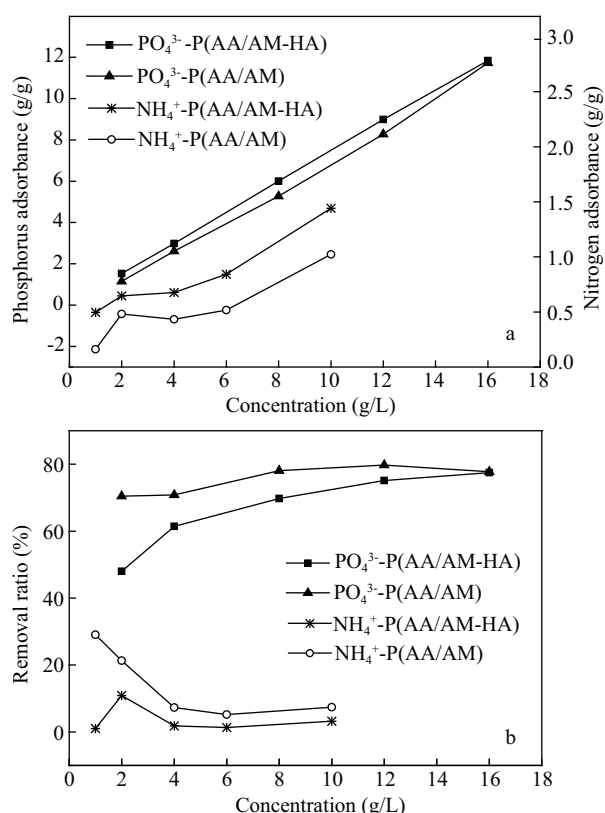


Fig. 6 Absorption (a) or desorption (b) of NH_4^+ , PO_4^{3-} on P(AA/AM-HA) and P(AA/AM).

2.2.3 Absorption of fertilizer

The absorption of NH_4^+ , PO_4^{3-} by superabsorbent is investigated and shown in **Fig. 6**. It can be seen from **Fig. 6a**, The absorption of NH_4^+ , PO_4^{3-} by P(AA/AM-HA) superabsorbent is superior to that of P(AA/AM), and the absorption of NH_4^+ , PO_4^{3-} were both below saturation. So P(AA/AM-HA) and P(AA/AM) has larger adsorption capacity for phosphate and ammonium. In **Fig. 6b**, the absorption of NH_4^+ , PO_4^{3-} by P(AA/AM-HA) is superior to that of P(AA/AM). In curve PO_4^{3-} -P(AA/AM-HA), the absorption of phosphate ion increases with the increase of phosphate concentration in the range of 2–12 g/L, and then decreases. The maximum removal ratio of phosphate ion is 79.5%. In curve NH_4^+ -P(AA/AM) and curve NH_4^+ -P(AA/AM-HA), the removal ratio of ammonium ion by P(AA/AM-HA) and P(AA/AM) decrease with the increase of ammonium concentration before 4 g/L, and then became stable. P(AA/AM-HA) is superior to P(AA/AM) on the absorption of ammonium ion. The absorption of NH_4^+ , PO_4^{3-} by P(AA/AM-HA) is much higher than that of P(AA/AM). This may be attributed to the fact that the functional groups of HA as well as acylamino and carboxyl functional groups interact with each other and cause a collaborative absorbent effect. At the same time, these functional groups of HA strongly complex with NH_4^+ , PO_4^{3-} (Su et al., 2007; Gou et al., 2006; Wu et al., 2008; Xie et al., 2012; Tyliczszak et al., 2009). The P(AA/AM-

HA) can effectively prevent NH_4^+ , PO_4^{3-} releasing which were used as fertilizer carrier.

3 Conclusions

The humic acid superabsorbent polymer (P(AA/AM-HA)) was synthesized. The optimum synthesis conditions are the weight ratio of MBA to AA and AM is 0.003; the weight ratio of KPS to AA and AM is 0.008; the weight ratio of HA to AA is 0.1; the mole ratio of AM to AA is 0.1; the mole ratio of NaOH to AA is 0.9 and reaction temperature 60°C. The water absorbency of the superabsorbent polymer was 1180 g/g, the half saturation time was 6.5 min, the 90% saturation time was 22 min and the saline absorbency was 110 g/g. The absorption of phosphate by P(AA/AM-HA) resin is superior to that of ammonium. The absorption of NH_4^+ , PO_4^{3-} by P(AA/AM-HA) is superior to that of P(AA/AM). P(AA/AM-HA) saturated with distilled water has network, lamellar and favaginous structure. The P(AA/AM-HA) superabsorbent has strong absorbing ability for water and fertilizer, better electrolytic tolerance and fewer cost than P(AA/AM) superabsorbent.

Acknowledgments

This work was supported by the University Innovation Team Project Foundation of Education Department of Liaoning Province (No. LT2010053) and the Open Foundation of Advanced Coal Coking Technology Key Laboratory of Liaoning Province.

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Journal of Environmental Sciences (Established in 1989)

Vol. 25 Supplement 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
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ISSN 1001-0742



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