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Sugarcane bagasse derivative-based superabsorbent containing phosphate rock with water–fertilizer integration

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ABSTRACT

To improve the water–fertilizer utilization ratio and mitigate the environmental contamination, an eco-friendly superabsorbent polymer (SPA), modified sugarcane bagasse/poly (acrylic acid) embedding phosphate rock (MSB/PAA/PHR), was prepared. Ammonia, phosphate rock (PHR) and KOH were admixed in the presence of acrylic acid to provide nitrogen (N), phosphorus (P) and potassium (K) nutrients, respectively. Impacts on water absorption capacity of the superabsorbent polymer (SAP) were investigated. The maximum swelling capacity in distilled water and 0.9 wt.% (weight percent) NaCl solution reached 414 g g^{-1} and 55 g g^{-1} (water/prepared SAP), respectively. The available NPK contents of the combination system were 15.13 mg g^{-1}, 6.93 mg g^{-1} and 52.05 mg g^{-1}, respectively. Moreover, the release behaviors of NPK in the MSB/PAA/PHR were also studied. The results showed that the MSB/PAA/PHR has outstanding sustained-release plant nutrients property.

1. Introduction

Superabsorbent polymers (SAPs) have been widely utilized in agriculture to reduce irrigation frequency, lower the death rate of plants and increase output of crops in arid belts (Abedi-Koupai, Sohrab, & Swarbrick, 2008). However, most of the SAPs are based on poly (acrylic acid) (PAA) which has poor biodegradability in soil. Now technological advancements associated with SAPs are expected to manufacture eco-friendly SAPs by using biodegradable natural materials. Considerable attention has been paid to the natural biodegradable resources such as starch, cellulose and chitosan (Athawate & Lele, 2001; Farag & Al-Afaleq, 2002; Nakason, Wohmang, Kaesaman, & Kiatkamjornwong, 2010). However, few reports have addressed sugarcane bagasse-based SAPs in agriculture.

Sugarcane bagasse (SB), the available waste material of alcohol and sugar industries, contains cellulose, hemicellulose and lignin (Sene, Converti, Felipi, & Zilli, 2002). Hydroxyl and phenolic groups is rich in SB, and these active groups can be modified easily to produce functional materials (Navarro, Sumi, Fujii, & Matsumura, 1996). Unfortunately, most of the SB are either burnt directly as fuel or disposed of in landfills (Burnham, 2010), resulting in enormous waste of natural resources and serious pollution. Recently, many studies on conversion and utilization of SB have been reported, including heavy metal adsorbent (Bassso, Cerrella, & Cukierman, 2002; Homagai, Ghimire, & Inoue, 2010; Karnitz et al., 2007; Navarro et al., 1996), biofuel (Mothe & de Miranda, 2009) and biochar (Inyang, Gao, Pullammanappallil, Ding, & Zimmerman, 2010). Due to the advantages of low-cost, abundance, renewability and biodegradability, SB can be used as skeletal materials to prepare economical and biodegradable superabsorbent. However, little attention has been paid to this new indication. Tetraethylenepentamine (TEPA) is a kind of alkaline–organic agent with large numbers of amino groups. In this study, SB was treated by alkali to break the lignin seal and disrupt the crystalline structure of cellulose (Aiello, Ferrer, & Ledesma, 1996). After introducing TEPA, the amino groups could significantly enhance the hydrophilicity of SB. Fertilizers and water are basic needs of plants, it is essential to integrate the supply of fertilizer and water in agriculture, especially in arid belts. During the past decades, the frequent excessive consumption of conventional fertilizers has caused severe environmental problem, such as fertilizer loss (Chen, 2001) and eutrophication of water (Bush & Austin, 2001; Daniel, Sharpley, & Lemunyon, 1998). Recently, great efforts have been focused on the sustained release fertilizers, such as physically mixed fertilizers, chemically combined fertilizers (Ray, Varadachari, & Ghosh, 1993) and coated fertilizers (Jarosiewicz & Tomaszewska, 2003; Mathews & Narine, 2010). However, most of these technologies achieved only slow-release of fertilizers but no water-retention (Al-Zahrani, 2000; Lamont, Worrall, & O'Connell, 1987). In order to reduce fertilizer loss rate, improve fertilizer bioavailability and mitigate

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the environmental pollution, the combination of superabsorbent polymers and fertilizers were developed in agricultural application (Chatzoudis & Rigas, 1998). However, the combination of SAPs and fertilizers still face great challenges. For instance, the higher ionic concentration originated from the dissolution of fertilizer restrains the polymerization process (Ward & Peppas, 2001) and reduces water absorption of the SAPs significantly. Moreover, most fertilizers are unstable and prone to discompose during the polymerization process under high temperatures and strong acid condition (Liang, Yuan, Xi, & Zhou, 2009). In the present study, to deal with the intractable these problems, superabsorbent was prepared by copolymerization of tetraethylenepentamine (TEPA) modified sugarcane bagasse (MSB) with acrylic acid, and the phosphate rock (PHR) was directly adopted as fertilizer to fill in modified sugarcane bagasse/poly (acrylic acid).

PHR is a kind of water-insoluble mineral with abundant resources, but is hard to be utilized by plants directly (Narayanasamy & Biswas, 1998). Some approaches have been employed to improve the phosphorous release of PHR, including microbial decomposition (Bhatti & Wasim, 2010), partial acidification (Biswas & Narayanasamy, 1998; Sengul, Ozer, & Sahin Gulaboglu, 2006) and dry compaction (Begum, Narayanasamy, & Biswas, 2004; Menon & Chien, 1996). However, the commercial potential and feasibility of these methods are not assured, moreover, the manufacture process of traditional water-soluble phosphorus fertilizer will bring about acid drainage, toxic heavy metal ions and fluoride-containing gas emission. If PHR can be directly used as fertilizer by superabsorbent polymer coating, the use of strong acid in manufacture of traditional water-soluble phosphate fertilizers will be exempted. This development will cut down acidic waste, as well as boost green manufacturing. As well known, PHR is prone to deposit during the polymerizing process, which makes it difficult to disperse and enwrap PHR in SAPs. Therefore, it is necessary to rely on the suspension and stabilization afforded by the swollen sugarcane bagasse derivatives to fill high content PHR in SAPs uniformly.

On the basis of the background above, we prepared a novel agricultural SAP based on modified sugarcane bagasse/poly(acrylic acid) embedding (PHR) to integrate the retention and sustained release of water and fertilizers into one system. The TEPA modified SB can suspend and disperse the phosphate rock (PHR) well in the polymerizing process. Moreover, acrylic acid was partially neutralized by KOH and ammonia solutions to introduce potassium and nitrogen to the SAP. The integration function was evaluated, and the results revealed that the system has several significant advantages over the conventional slow release fertilizers and traditional agricultural SAPs which generally have only one function.

2. Materials and methods

2.1. Materials

Sugarcane bagasse (SB, collected from local juice workshop in Guangzhou, China) used as raw materials was milled and dried at 105 °C for 12 h, and then sieved through a 100 mesh screen. TEPA (C.R.) was purchased from Guanghua Chemical Factory Co., Ltd (Guangdong, China). Acrylic acid (AA, A.R.), potassium persulfate (KPS, A.R.) and N,N′-methylenebisacrylamide (NMBA, A.R.) were obtained by Tianjin Kermel Chemical Reagent Co., Ltd (Tianjin, China). AA was distilled under reduced pressure before use. PHR (total phosphorus is 22.9%, purchased from Zhongxiang Co., Ltd (Hunan, China)) was milled through a 200-mesh screen before use. Other agents were all of analytical grade and all the solutions were prepared in distilled water.

2.2. Modification of sugarcane bagasse

Firstly, sugarcane bagasse (10.0 g) was weighed and dipped in a 500 mL beaker with 20% sodium hydroxide solution. The aqueous suspension was stirred at room temperature for 1 h and left for overnight, then was filtered and washed with distilled water repeatedly until the pH of eluate reached 8–9. The filter residue was collected for further use. After alkali-treatment, the swelling property of the sugarcane bagasse cellulose was enhanced, thus the active sites were increased. This residue obtained above is referred as basified sugarcane bagasse (BSB).

10.0 g of dried BSB was added into a 500 mL three-necked round-bottom flask equipped with a thermometer, a condenser and a magnetic stirrer, followed by adding 200 mL of alcohol (reaction medium) and 40 mL of chloroepoxy propane. The whole equipments were put into oil bath and the reaction was sustained for 24 h at 60 °C. In this way, the epoxy groups with high activity were introduced after the etherification reaction of BSB and chloroepoxy propane. The product, etherified sugarcane bagasse (ESB), was obtained.

Afterwards, 40 mL of TEPA was dropped slowly into ESB mixture and kept on reacting for 24 h at 60 °C. The TEPA modified sugarcane bagasse (MSB) was synthesized by nucleophilic substitution reaction of ESB and TEPA. MSB was obtained after the final reaction product was filtered and washed with alcohol. Finally, the MSB was dried under vaccum at 60 °C for 12 h. The modification process is depicted in Fig. 1.

2.3. Preparation of MSB/PAA/PHR

The MSB/PAA/PHR was prepared by solution polymerization. At first, dried MSB (2.0 g) dispersed in distilled water (35 mL) mixing with PHR (3.0 g), was added into a 500 mL three-necked round-bottom flask equipped with a thermometer, a condenser and a magnetic stirrer. The mixture was stirred for 30 min at room temperature in a water bath. During this process, the PHR can be availably suspended, dispersed and coated by the swollen MSB. Then, AA (10.0 g) was partially neutralized by KOH and ammonia solution (2.72 g KOH and 3.31 g 25 wt.% ammonia were dissolved in 25 mL distilled water, the calculated mole ratio of K to N was 1:1), and 1.9 wt.% KPS (related to AA) and 0.5 wt.% NMBA (related to AA) were added to the partly neutralized AA solution. The AA solution was added to the MSB/PHR mixture solution described above under the magnetic stirring. The water bath was heated slowly to 75 °C and incubated for 3 h to complete the polymerization. Then the resulting product was washed several times with ethanol and dried at 70 °C to a constant weight. And the dried product was milled to 20 mesh for further use.

2.4. Characterization

The SB, MSB and MSB/PAA/PHR were characterized by Fourier transform infrared (FTIR) spectroscopy analysis. The performance was carried out on Nicolet 6700 FT-IR (Thermo Nicolet, USA). The holocellulose, α-cellulose (cellulose) and hemicelluloses content were determined according to the methods of the American National Standard Institute (1974). The holocellulose contains α,β,γ-cellulose and hemicelluloses.

2.5. Measurement of water absorbency of the MSB/PAA/PHR

0.2 g of dry sample was put into a 200-mesh fastened nylon bag. Then, the bag was immersed in distilled water (or 0.9 wt.% NaCl solution) for 24 h to reach the swelling equilibrium at room temperature. Subsequently, the bag was lifted out. After wiping off the residual water by filter paper, the bag was weighed. The

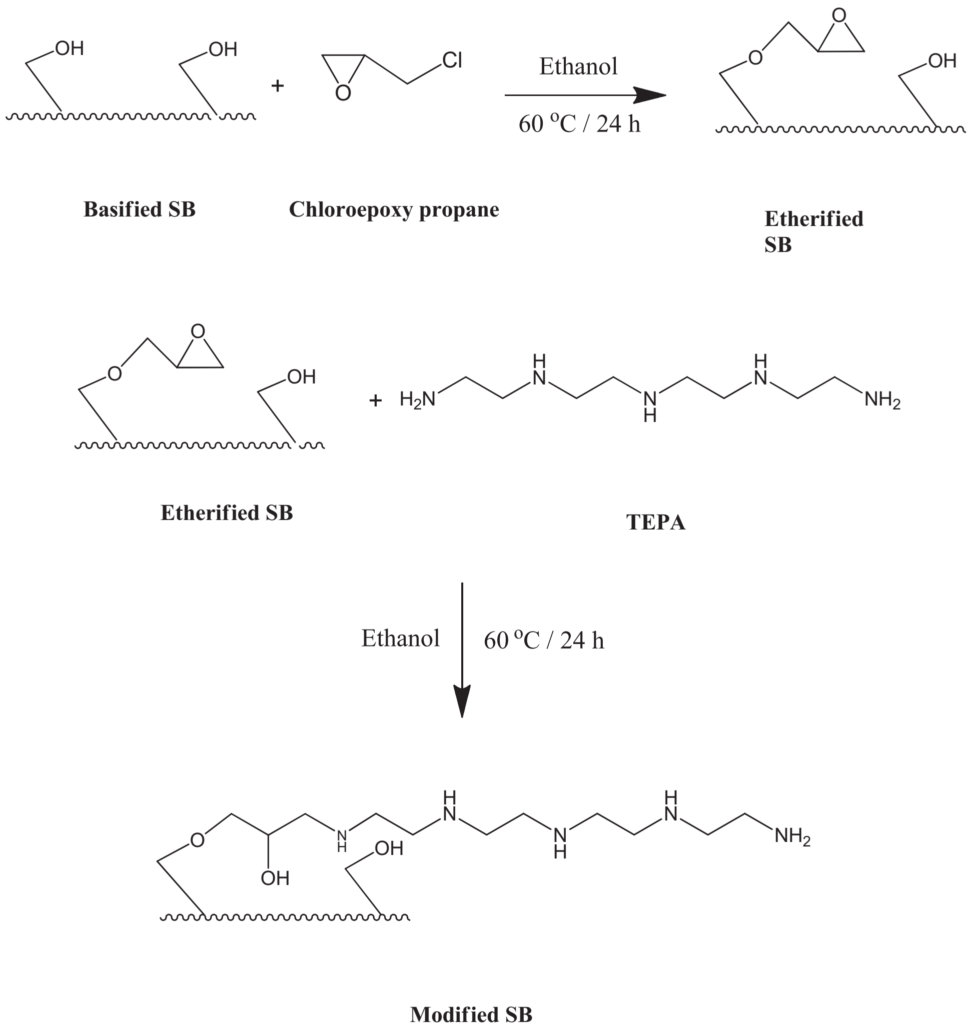

Fig. 1. The schematic representation of synthetic process of MSB.

water absorbency Q_{eq} (H_2O) of the MSB/PAA/PHR was calculated by Eq. (1):

$$Q_{eq}\ (H_2O) = \frac{m_c - m_b - m_a}{m_b} \tag{1}$$

where m_a, m_b and m_c are the weights of the wet nylon bag, the dry sample and the swollen sample, respectively. All the experiments were carried out for three times to obtain the average values.

2.6. Measurement of the NPK content in MSB/PAA/PHR

The ammonium nitrogen content in MSB/PAA/PHR was measured by indophenol blue colorimetric method (Lu, 1999). In alkaline solution, NH_4^+ reacted with hypochlorite and phenol to form stable water-soluble indophenol blue. When the solution contains 0.05–0.5 mg L^{-1} nitrogen, the color depth of the indophenol is proportional to the consistence of nitrogen. The absorbance was performed at the wavelength of 625 nm using UV–vis spectrophotometer (model UV 2300, Tian Mei Co., Ltd., China).

The available phosphorus content in MSB/PAA/PHR was determined by phosphorus vanadium molybdate yellow colorimetric method (Lu, 1999). In acid solution, phosphorus reacted with vanadium ammonium molybdate to form molybdophosphate in the absence of F^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ interference. The color depth of the complexes is proportional to the content of phosphate when the solution contains 0–0.1 mg L^{-1} phosphate. The available phosphorus of the sample was extracted by using 20 g L^{-1} citric acid solution, and the absorbance was performed at the wavelength of 420 nm by UV–vis spectrophotometer (model UV 2300, Tian Mei Co., Ltd., China).

The water-soluble phosphorus content in MSB/PAA/PHR was measured by Mo–Sb colorimetry (Lu, 1999). In acid solution, phosphorus reacted with ammonium molybdate to form a molybdophosphate. Then, the molybdophosphate was reduced by ascorbic acid to form a blue complex (phosphomolybdenum blue) in the presence of oxygenpotassium antimonyl tartrate. The color depth of the complex is proportional to the concentration of phosphate, and the absorbance was determined at the wavelength of 700 nm on UV–vis spectrophotometer (model UV 2300, Tian Mei Co., Ltd., China).

The water-soluble potassium content in MSB/PAA/PHR was measured by flame photometry (model 6400A, Shanghai Precision and Scientific Instrument Co., Ltd., China).

2.7. Sustained release behaviors of the MSB/PAA/PHR

0.2 g of dry MSB/PAA/PHR and 0.2 g of PHR were added in two separate flasks containing 250 mL of distilled water (release medium), respectively, to study the release behaviors of NPK. Then the flasks were put into a water jacket incubator, and the temperature was set at 25 °C. At particular intervals of time (2 h, 4 h, 6 h, 8 h, 10 h, 1 d, 3 d, 5 d, 7 d, 9 d, 11 d, 13 d and 15 d), 25 mL of extracted

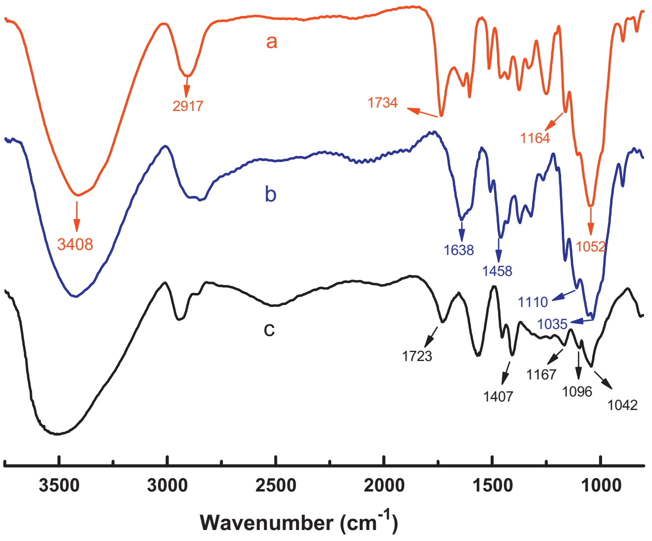

Fig. 2. The FTIR spectra of (a) SB, (b) MSB, (c) MSB/PAA/PHR.

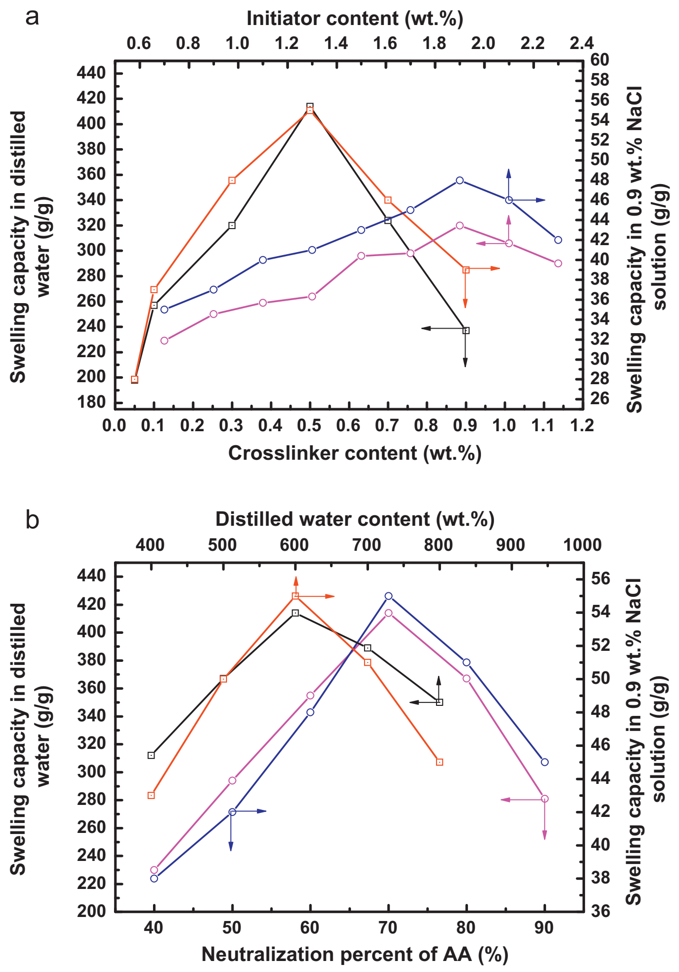

Fig. 3. Impacts on the water absorbency. (a) Effects of the initiator and crosslinker content on the water absorbency. $T = 75\,^{\circ}\mathrm{C}$, MSB = 2.0 g, AA = 10 g, PHR = 3 g, Neutralization percent of AA = 70%. (b) Effects of the distilled water content and neutralization percent of AA on the water absorbency. $T = 75\,^{\circ}\mathrm{C}$, MSB = 2.0 g, AA = 10 g, PHR = 3 g, KPS = 1.9 wt.%, NMBA = 0.5 wt.%.

fluid was sampled for NPK measurement, then an additional 25 mL of distilled water was added into the flask to maintain a constant volume of solvent. The release ratios of nitrogen (N%), phosphorus (P%) and potassium (K%) were calculated by the following Eq. (2):

$$\begin{aligned} \mathrm{N\%} &= 100\% \cdot m_1/m_0 \\ \mathrm{P\%} &= 100\% \cdot m_3/m_2 \\ \mathrm{K\%} &= 100\% \cdot m_5/m_4 \end{aligned} \qquad (2)$$

where m_0, m_2 and m_4 are, respectively, the weights of the total nitrogen, total phosphorus and total potassium. m_1, m_3 and m_5 are the weights of ammonium nitrogen, water-soluble phosphorus and water-soluble potassium in extracted fluid.

3. Results and discussion

3.1. Characterization

The holocellulose, α-cellulose (cellulose) and hemicelluloses content of SB were 59.7%, 42.6% and 6.2%, respectively. After the mercerization treatment, the remaining mass of SB was found to be 38.7% of the initial mass, and the cellulose content is 97.8% (cellulose: mercerized SB). The amount of cellulose of mercerized SB is smaller than that of SB, which is attributed to the decomposition and remove of the small fraction of cellulose by alkali.

The FTIR spectra of SB, MSB and MSB/PAA/PHR are shown in Fig. 2. In the FTIR spectrum of SB (Fig. 2(a)), the band at 3408 cm^{-1} ascribes to the —OH stretching vibration of the groups in cellulose. The absorption bands at 2917 cm^{-1} and 1734 cm^{-1} attribute to C—H stretching and C═O stretching vibration of the glucose unit, respectively. Additionally, the absorption bands at 1052 cm^{-1} and 1164 cm^{-1} belong to C—O—C symmetric stretching and asymmetric stretching vibration of cellulose, respectively. Fig. 2(b) displays the FTIR spectrum of MSB, the band at 1734 cm^{-1} (C═O stretching vibration) disappears after modification, which reveals that the sugar residues have been removed during the basified treatment. Moreover, new absorption bands at 1638 cm^{-1} (N—H deformation vibration), 1110 cm^{-1} and 1035 cm^{-1} (N—C stretching vibration) are observed after modification, and the intensity of absorption band of C—H deformation vibration (1458 cm^{-1}) is much more intense than that of SB. These changes verify that SB has been conjugated with TEPA successfully. Fig. 2(c) is the FTIR spectrum of MSB/PAA/PHR, by comparing with Fig. 2(b), the polymerization of AA is confirmed by the appearance of absorption bands at 1723 cm^{-1} (C═O stretching vibration) and 1407 cm^{-1} (O—H deformation vibration). Besides, the appearance of absorption bands at 1167 cm^{-1} (P═O stretching vibration), 1096 cm^{-1} and 1042 cm^{-1} (P—O stretching vibration) prove that PHR is bound by the polymer successfully.

3.2. Effects of the initiator and crosslinker content on the water absorbency

The effects of the initiator and crosslinker content on the water absorbency of the prepared MSB/PAA/PHR were studied with various contents of KPS and NMBA, which were referred as the weight percents of the initiator and crosslinker to AA. The result is shown in Fig. 3.

The feed ratio of initiator has shown the remarkable impacts on the polymerization process. It can be observed in Fig. 3(a) that the maximum water absorbency is obtained at 1.9 wt.% initiator content. A further augment or decrease of initiator content causes the decline of water absorbency. The reason may lie in that the initiator is mostly consumed in producing a large number of growing polymer chain when the initiator content is low (Athawate & Lele, 2000). Therefore, with the increase of initiator content from 0.7 wt.% to 1.9 wt.%, the formed network structure becomes more and more stable, thus the water absorption capability is increased

Table 1
Effect of PHR content on available phosphorus, water-soluble phosphorus content and water absorbency. $T = 75\,^{\circ}\mathrm{C}$, KPS = 1.9 wt.%, NMBA = 0.5 wt.%, MSB = 2.0 g, AA = 10.0 g, Neutralization percent of AA = 70%.

PHR content[a] (wt.%)	Total phosphorus[b] ($\mathrm{mg\,g^{-1}}$)	Available phosphorus[c] ($\mathrm{mg\,g^{-1}}$)	Water-soluble phosphorus[d] ($\mathrm{mg\,kg^{-1}}$)	Q_{eq}[e] ($\mathrm{g\,g^{-1}}$)	Q_{eq}[f] ($\mathrm{g\,g^{-1}}$)
0	0	0	0	389	49
10	13.09	2.67	8.05	414	55
20	24.76	4.97	15.13	376	51
30	35.23	6.93	21.34	324	45
40	44.68	8.52	25.91	261	42
50	53.26	9.85	29.76	220	37

[a] Selected according to the weight of AA.
[b] Theoretical value of total phosphorus, shown by P_2O_5:MSB/PAA/PHR.
[c] Measured value of available phosphorus, shown by P_2O_5:MSB/PAA/PHR.
[d] Measured value of water-soluble phosphorus, shown by P_2O_5:MSB/PAA/PHR.
[e] Water absorbency in distilled water.
[f] Water absorbency in 0.9 wt.% NaCl.

continuously. However, when initiator content exceeds 1.9 wt.%, the rush out of plethoric free-radicals causes popcorn polymerization and terminating step due to the heat accumulation originated from the too fast polymerization, accompanying by low molecular weight SAP and weak water absorption capacity.

The crosslinker content is the most significant influencing factor on the water absorbency. As shown in Fig. 3(a), the water absorbency increases with the augment of crosslinker content from 0.05 wt.% to 0.5 wt.%, but declines with the excess crosslinker content. The result can be explained by Flory's expansion theory (shown in Eq. (3)) (Flory, 1953):

$$Q_{eq}^{3/5} \cong \frac{\left((1/2)\times(i/V_u)\times(1/s)^{1/2}\right)^2 + \left((1/2)-X_1\right)/V_1}{V_e/V_0} \qquad (3)$$

where Q_{eq} is the water absorbency of polymers, and i is the charge number in each polymerized unit of the polyelectrolyte. S is the ionic strength of the external solution. V_u is the volume of the molecular unit. X_1 is the parameter of binding free energy between solvent and polymer. V_e is the number of effective network chains in adsorption and V_o is the volume of the relaxed network parameter. It can be inferred that $((1/2)\times(i/V_u)\times(1/S)^{1/2})^2$ and $((1/2)-X_1)/V_1$ represent the osmotic pressure difference and the hydrophilic property of the SAP, respectively, and V_e/V_o stands for the density of the effective network chains in adsorption. In the present study, when the crosslinker content is more than 0.5 wt.%, with the augment of crosslinker content, the crosslinking density is increased and the network space gets compact, bringing about the decline of water absorbency. Similar observation was reported by the previous work of Li, Wang, and Chen (2004) and Chen and Zhao (1999).

3.3. *Effects of the water content and neutralization percent of AA on the water absorbency*

Water absorption capacity of the MSB/PAA/PHR is related to the charge density in the polymeric network, which is affected by the neutralization percent of AA. As depicted in Fig. 3(b), the maximum water absorbency is 414 $\mathrm{g\,g^{-1}}$ in distilled water and 55 $\mathrm{g\,g^{-1}}$ in 0.9 wt.% NaCl solution is achieved at 70% neutralized, while a further augment or decrease of neutralization percent results in the decline of water absorption capacity. This is attributed to the fact that the liquid absorbency is affected by the osmotic pressure difference according to Eq. (3). When the neutralization percent of AA increases from 50% to 60%, the amount of K^+ and NH_4^+ ions rise, which leads to the enhancement of the ionic strength in the polymeric network, followed by the improvement of osmotic pressure difference and water absorption capacity. However, when the neutralization percent of AA is excess 70%, the void space, which is originated from the mutual repulsion of $-COO^-$ groups, will be reduced by the overmuch bonded K^+ and NH_4^+ ions in the polymeric network. As a result, the water absorption decreased severely.

The effect of feeding water content (related to AA) on the water absorbency was investigated. Fig. 3(b) depicts that the maximum water absorbency is achieved when feeding water content is 600 wt.%, and a decline of absorbency will result from a further increase or decrease of water content. The reason lies in that the inadequate water content causes a high density of AA, NMBA and KPS, resulting in excessive intense polymerization and close-knit polymeric network, which lead to the compression of void fraction for penetrating water and lower water absorption capacity. On the contrary, AA, NMBA and KPS become widely separate in aqueous solution when the water content is excessive. Consequently, the copolymerization cannot be finished fully and the product is semiliquid, resulting in a serious decline of water absorption capacity.

3.4. *Effect of PHR content on the water absorbency*

The feeding amount of PHR plays a key role in impacting water absorbency of the superabsorbent (depicted in Table 1). The water absorbency of the MSB/PAA/PHR increases with the rising PHR content (weight percent related to AA) when the amount of PHR is less than 10 wt.%. This phenomenon may because the fact that the $-OH$ on the surface of PHR such as $Ca_{10}(PO_4)_6(OH)_2$, could react with acrylic acid, which could reinforce the hydrophilicity of the polymeric network, and then improve the water absorption. However, further increase of feeding PHR from 10 wt.% to 50 wt.% brings about a sharp decrease of the water absorption. This can be explained as follows: the overdose PHR results in the generation of excessive crosslink points in the polymeric network, which will cause overstocked crosslink density of the SAP and poor water absorbency. In addition, since water soluble phosphate contained in PHR will dissociate positive ions Ca^{2+} and negative ions $PO_4{}^{3-}$, Ca^{2+} will chelated the negative charged $-COO^-$ groups of the poly(acrylic acid) network and abate their water affinity, resulting in the decrease of osmotic pressure difference and lower water absorption capacity. Moreover, when the blended PHR is excessive, the redundant PHR cannot be enwrapped efficiently by SAP and congests in the void or inter-space of polymeric network, which hinders water pervasion and leads to the decline of water absorption capacity.

3.5. *The NPK content in MSB/PAA/PHR*

The results of the available phosphorus and water-soluble phosphorus content in MSB/PAA/PHR are exhibited in Table 1. Both of them increase with the augment of the feeding PHR content. However, the growth rate of available phosphorus and water-soluble phosphorus amount is much lower than that of the feeding

Table 2
Effect of neutralization percent of AA on ammonium nitrogen and water-soluble potassium content in the MSB/PAA/PHR.

Neutralization percent of AA[a]	Ammonium nitrogen[b] (mg g^{-1})	Water-soluble potassium[c] (mg g^{-1})
40%	8.50	30.68
50%	10.91	36.15
60%	13.13	44.35
70%	15.13	52.05
80%	16.58	58.80
90%	17.86	67.52

[a] AA was partially neutralized by KOH and ammonia solutions (mole ratio of K:N = 1:1).
[b] Shown by N: MSB/PAA/PHR.
[c] Shown by K: MSB/PAA/PHR.

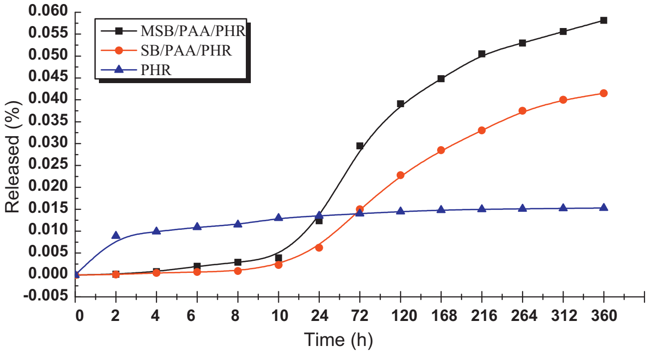

Fig. 4. Comparison of the phosphorus release between PHR, MSB/PAA/PHR and SB/PAA/PHR. AA = 10 g, PHR = 3 g, MSB (SB) = 2 g.

PHR content. This may because when the enclosed PHR need the dispersion and stabilization afforded by the swollen MSB in the process of polymerization, when the feeding PHR content is too high, the plethoric PHR cannot be suspended and stabilized effectively, resulting in a mass of deposit in the polymerization solution. Therefore, the filled PHR content in the MSB/PAA/PHR is lower than the presupposed PHR content.

Table 2 depicts the ammonium nitrogen and water-soluble potassium content in the MSB/PAA/PHR with different neutralization percent of AA. Both N and K content increase with the augment of the neutralization percent of AA. Since almost all of the water-soluble potassium is originated from the KOH solution and without any loss during the polymerization process, the water-soluble potassium content is nearly proportional to the neutralization percent of AA. In comparison, ammonia is volatile under higher temperature, which may cause a great loss during the polymerization, thus the increment of ammonium nitrogen is unconspicuous.

Considering the comprehensive advantage of water absorbency and NPK content, 30 wt.% of PHR content with 70% neutralization percent of AA is regard as the optimal option. In such case, the optimal synthesis conditions are displayed as below: the content of initiator, crosslinker, PHR, distilled water and neutralization percent of AA were 1.9 wt.%, 0.5 wt.%, 30 wt.%, 600 wt.% and 70%, respectively. The water absorbency of the MSB/PAA/PHR in distilled water and 0.9 wt.% NaCl solution reached 324 g g^{-1} and 45 g g^{-1}, respectively, while the available phosphorus, water-soluble phosphorus, ammonium nitrogen and water-soluble potassium content of the MSB/PAA/PHR were 6.93 mg g^{-1}, 21.34 mg kg^{-1}, 15.13 mg g^{-1} and 52.05 mg g^{-1}, respectively.

3.6. Effect of the modification of sugarcane bagasse on the release of water-soluble phosphorus

The release behaviors of water-soluble phosphorus of PHR, MSB/PAA/PHR and SB/PAA/PHR are displayed in Fig. 4. It is well known that water-soluble phosphorus can be dissolved in water easily, so the release of PHR shows a typical first-order release behavior: an initially high release rate followed by a rapidly declining release rate, more than 90% of water-soluble phosphorus in PHR was released within 4 h. Moreover, the released phosphorus in PHR only originated from the soluble part of the PHR, and the insoluble part cannot be released, so the release ratio of phosphorus is very low. However, since the swollen hydrogel network is capable of reducing the release rate of water-soluble phosphorus, for the SB/PAA/PHR and MSB/PAA/PHR, the water-soluble phosphorus showed a preferable sustained-release property. Moreover, the release ratios of phosphorus in SB/PAA/PHR and MSB/PAA/PHR are much higher than that of PHR after 72 h, the reason may be that some of the insoluble PHR is dissolved by the acidic microenvironment in the swollen PAA. Detailedly, after 15 days, the release ratio of phosphorus in MSB/PAA/PHR has increased by about 40% and 280% over the SB/PAA/PHR and PHR, respectively. The discrepancy implies that the modification of sugarcane could greatly improve the amount of the released phosphorus. Being a kind of hydrophilic natural polymer modified by polyamine, swollen MSB can form a pasty viscous soliquoid, which benefits the suspension stability and dispersion uniformity of PHR in polymerization solution, and then reduce the deposit amount of PHR during the polymerizing process. Moreover, the introduced TEPA can be chelated with Ca^{2+}, thereby change the ionization equilibrium of the insoluble $Ca_3(PO_4)_2$ (the key component of PHR) and improve the release amount of water-soluble phosphorus. However, the raw SB cannot swell to suspend and disperse PHR, and can hardly reduce the deposit of PHR in the polymerization solution. Therefore, the sustained release amount of water-soluble phosphorus of the final product is much lower.

In general, to render PHR into water-soluble phosphate is the essential process to produce phosphate fertilizer in traditional factory. However, this produce process consumes a great deal of strong acid. The present work illustrates that this is not the only way which must be passed to produce PHR water-soluble to feed crops phosphorus. On the contrary, the fertilizer utilization of PHR in a water-insoluble state can avoid the pollution of water-soluble hazardous heavy metal ions such as Cd^{2+}, Pb^{2+}, which is originated from the strong acid dissolving water-insoluble salts/oxides of heavy metals in associated minerals during the traditional manufacture of phosphate fertilizer.

3.7. Sustained release of NK from the MSB/PAA/PHR in water

Fig. 5 depicts the sustained release behaviors of ammonium nitrogen and water-soluble potassium in MSB/PAA/PHR. As

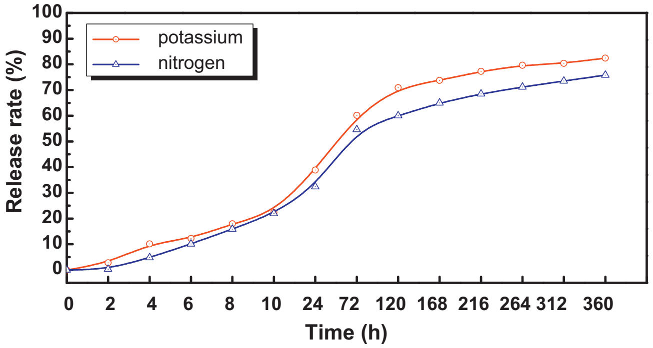

Fig. 5. The release behaviors of ammonium nitrogen and water-soluble potassium, PHR = 3 g, KOH = 4.67 g, neutralization percent of AA = 70%.

expected, these two nutrients had shown a sustained release property in 15 days.

Comparing with water-soluble phosphorus in Fig. 4, it is obvious that the release rate of N and K are much faster than that of P in the early period. The discrepancy could be explained as follows: the released N and K originate from the water soluble NH_4^+ and K^+ ions which are mainly adsorbed by carboxyl groups of the polymeric network through electrostatic interaction, and both NH_4^+ and K^+ ions could be easily ionized in water and released out. At the beginning of the release period, the N and K were quickly exhausted due to the high concentration difference between the MSB/PAA/PHR and the outside water. Subsequently, the release rate decreased rapidly as the amount of NH_4^+ and K^+ ions had been exhausted. Comparing with the release rate of nitrogen and potassium, the total releases of phosphorus in MSB/PAA/PHR did not exceed 50 wt.% by the third day. Since the main component of the PHR is insoluble phosphates and the water-soluble phosphorus content is very low. During the first 72 h, most of the water-soluble phosphorus was released by the dynamic exchange between the free water in the MSB/PAA/PHR and the water outside. Then, the release rate of water-soluble phosphorus decreased but still kept a higher release rate. This could be ascribable to the fact that some of the insoluble phosphate in PHR has been dissolved to be water soluble phosphorus by the corrosion of poly(AA). This result suggests that, in the MSB/PAA/PHR, the retained release capability of phosphorus is much better than that of water soluble nitrogen and potassium. A deduction could be claimed that water insoluble PHR is more suitable to combine with MSB/PAA to prepare long term sustaining release fertilizer than other water-soluble commercial fertilizers.

4. Conclusions

In this study, a novel eco-friendly agricultural SAP based on modified sugarcane bagasse/poly (acrylic acid) embedding phosphate rock (PHR) was prepared and the integrating function of water and fertilizer supply was investigated. The results showed that the product had excellent water absorption capacity and preferable sustained release property. The utilization of natural resource such as sugarcane bagasse and phosphate rock in the production of SAP could significantly reduce the production cost and mitigate the environmental contamination. In summary, this new combining system is expected to have wide application in agriculture and horticulture, particularly in the arid region.

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