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Starch derivative-based superabsorbent with integration of water-retaining and controlled-release fertilizers

Kang Zhong[1], Zuan-Tao Lin[1], Xi-Liang Zheng, Gang-Biao Jiang*, Yu-Sheng Fang, Xiao-Yun Mao*, Zong-Wen Liao

College of Natural Resource and Environment, School of South China Agricultural University, Guangzhou 510642, China

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ABSTRACT

Phosphate rock (PHR), a traditional fertilizer, is abundant, but is hard to be utilized by plants. To improve the utilization of PHR, and to integrate water-retaining and controlled-release fertilizers, an agricultural superabsorbent polymer based on sulfonated corn starch/poly (acrylic acid) embedding phosphate rock (SCS/PAA/PHR) was prepared. PHR can be suspended and well-dispersed in SCS/PAA by sulfonated corn starch (SCS). PHR and KOH were mixed in acrylic acid solution to provide phosphorus (P) and potassium (K) nutrients, respectively. Impacts on water absorption capacity of the superabsorbent were investigated. The maximum swelling capacity in distilled water or 0.9 wt.% (weight percent) NaCl solution reached 498 $\mathrm{g\,g^{-1}}$ and 65 $\mathrm{g\,g^{-1}}$ (water/prepared dry superabsorbent) respectively. Moreover, release behaviours of P and K in SCS/PAA/PHR were also investigated. The results showed that SCS/PAA/PHR possessed excellent sustained-release property of plant nutrient, and the SCS/PAA could improve the P release greatly. Besides, the XPS analysis was employed to study the relationship between PHR and superabsorbent polymer.

1. Introduction

More than 7 billion people depend on modern agriculture. China has 1.3 billion people, and the population is still growing, but there is only 7% of world's arable land which is available in China. In past decades, drought, one of the most severe representations of global climate change in China, occured frequently; the problems of river runoff and water resources also played a negative role on crop production. Population growth, climate change and extreme climate occurrence frequently associated with drought, have given rise to a new area, namely, eco-friendly agriculture. Sufficient water supply is a key condition for plant growth, however, it is not enough to sustain the plant growth only by offering water because the fertilizer can promote the plant growth, resulting in the good utilization of water by plant. Therefore, fertilizer and water are two essential requirements of plant growth, and it is essential to integrate the adequate supply of fertilizer and water in agriculture, especially in those areas which are suffering from drought (Ni, Liu, Lü, Xie, & Wang, 2011; Piao et al., 2010; Tilman, Cassman, Matson, Naylor, & Polasky, 2002; Vassilev, Vassileva, Fenice, & Federici, 2001).

Superabsorbent polymer (SAP), which can absorb, retain large amount of water and slow release them in dry circumstance, has been utilized extensively in various fields (Marcì, Mele, Palmisano, Pulito, & Sannino, 2006; Nykänen, Nykänen, Puska, Goulart Silva, & Ruokolainen, 2011; Omidian, Rocca, & Park, 2005; Wang & Wang, 2010). In agriculture, they have been successfully employed to reduce irrigation frequency, and decline the death rate of plants, as well as increase the output of crops in arid/semi-arid lands. In practice, however, it always increases farmers' financial burden, but does not significantly bring an augment of the crops yield if SAP is utilized without supply of fertilizers. Recently, sustained release fertilizers, including physically mixed fertilizers, chemically combined fertilizers (Chandra, Ghosh, & Varadachari, 2009; Jarosiewicz & Tomaszewska, 2003; Prasad, Rajale, & Lakhdive, 1971; Ray, Varadachari, & Ghosh, 1993) and coated fertilizers (Liang, Yuan, Xi, & Zhou, 2009; Mathews & Narine, 2010; Ni, Liu, & Lü, 2009; Teodorescu, Lungu, Stanescu, & Neamtu, 2009; Wu & Liu, 2008; Wu, Liu, & Liang, 2008), have attracted prevail attention. However, many of these sustained release technologies only achieve slow-release of fertilizers, but not water-retention, such as polyethylene, paraffin and resin coated fertilizers (Al-Zahrani, 2000). Nevertheless, the additive cost is not inexpensive. Hence, it is important to develop an economic control-released fertilizer with water-retention. More recently, Ni et al. reported a slow-release nitrogen fertilizer coated chemically modified cellulose hydrogel which is designed to control nutrient release and improve the water-retaining ability of soil. However, it is also obvious that its water swelling capacity is limited, and hydrogel degradation is rapid (Ni et al., 2011). Wu et al. prepared a double coated fertilizer which contain the out coating

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* Corresponding authors. Tel.: +86 20 85280293; fax: +86 20 85280292.
E-mail address: jgb3h@163.com (G.-B. Jiang).

[1] These authors contributed equally to this work.

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(P(AA-co-AM)) and inner coating (chitosan) (Wu & Liu, 2008). But the limit is its high cost.

On the other hand, the combination of SAP and fertilizers also still face many challenges, for instance, most fertilizers, e.g. urea, is prone to decompose in acrylic acid (AA) which is the most widely used monomer of SAP. Moreover, the higher ionic concentration originated from the dissolution of fertilizers inhibits the polymerization of monomers and decrease water absorption of the SAP. The most of sustained fertilizers research focus on N fertilizers, but few report concerns on other fertilizers such as phosphorous.

Phosphate rock (PHR), a natural mineral with rich resource, is hard to be utilized directly by plants (Narayanasamy & Biswas, 1998). Some approaches have been used to improve Phosphorous release of PHR, including partial acidification (Biswas & Narayanasamy, 1998; Sengul, Ozer, & Sahin Gulaboglu, 2006) and dry compaction (Menon & Chien, 1996). However, these methods are limited due to their low feasibility in industry. If PHR can be directly exploited by superabsorbent coating to obtain integration of water-retaining and fertilizers, and amount of release of water-soluble Phosphorous can be improved, it will not only reduce the manufacture expense, but avoid the consuming of phosphoric acid or sulfuric acid in producing phosphate fertilizers.

As a traditional fertilizer, PHR is directly used in soil. Generally, the content of available phosphorus (comprises water-soluble phosphorus and citric acid soluble phosphorus) in PHR is only about 5%, but the content of water-soluble phosphorus in PHR is only 32 mg kg^{-1}, it means that the amount of phosphorus which the plant can be directly used is very small, and more amount of water-soluble phosphorus release must rely on the acid of certain type of soil, some microorganism or special enzymes that exist in soil. Therefore, the water-insoluble trait of PHR limits its directly application. Besides, PHR is prone to deposit during the polymerizing process, which makes it difficult to disperse and enwrap PHR in SAP. In our previous study, a novel superabsorbent polymer, modified sugarcane bagasse/poly (acrylic acid) embedding phosphate rock (MSB/PAA/PHR) was prepared (Zhong, Zheng, Mao, Lin, & Jiang, 2012). The PHR can be suspended during the polymerizing process by modified sugarcane bagasse (MSB), and the experimental results indicate that release of phosphorus is improved obviously.

In this work, sulfonated corn starch and PHR were combined with poly (acrylic acid) to prepare an agricultural superabsorbent. The water-solubility of sulfonated corn starch is much better than that of MSB, thus the sticky solution originated from sulfonated starch can suspend and stabilize the PHR much better than MSB. In addition, the sulfonated starch has acid property, while the MSB does not, so the amount of water-soluble phosphorus release can be improved much more than that of MSB/PAA/PHR due to the acid of sulfonated corn starch. Moreover, sulfonated corn starch can increase the absorbency of water in soil with high saline concentration, because the introduced sulfonated anions can increase charge density and ionization tendency of the SCS/PAA/PHR (Lim, Wang, Yoon, & Ko, 2001). The maximum amount of water-soluble phosphorus release in SCS/PAA/PHR is 42.51 mg kg^{-1}, while that of MSB/PAA/PHR is 29.76 mg kg^{-1}. The maximum amount of water-retaining ability of SCS/PAA/PHR is 498 g g^{-1}, while that of MSB/PAA/PHR is 414 g g^{-1}(Zhong et al., 2012). Thus, the amount of water-soluble phosphorus release and water-retaining ability of SCS/PAA/PHR would be higher than that of MSB/PAA/PHR.

In this paper, we prepared a novel agricultural SAP based on sulfonated corn starch/poly (acrylic acid) embedding PHR to integrate the retention and sustained release of water and fertilizers. This SAP is characterized by FTIR. Besides, we first employ the XPS analysis to study the relationship between PHR and superabsorbent polymer. The water absorbency in different conditions and sustained release behaviours are investigated.

2. Materials and methods

2.1. Materials

The corn starch (CS) used was obtained from Guangzhou Xincheng Chemical Co. Ltd. (Guangdong, China). Chlorosulfonic acid used as the sulfonating agent was purchased from Guanghua Chemical Factory Co. Ltd. (Guangdong, China). Acrylic acid (AA), potassium persulfate (KPS) and *N*,*N*′-methylenebisacrylamide (NMBA) was offered by Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China). PHR (total phosphorus was 22.9%, purchased from Zhongxiang Co. Ltd. (Hunan, China)) was milled through a 200-mesh screen before use. Other agents used were all of analytical grade.

2.2. Preparation of sulfonated corn starch

Sulfonated corn starch (SCS) was prepared according to a previously reported method (Cui, Liu, Wu, & Bi, 2009). 200 mL of Pyridine was added to a 500 mL three-necked round-bottom flask equipped with a dropping funnel, a thermometer, a condenser and a magnetic stirrer. Then, 10 mL of chlorosulfonic acid was dropped slowly into the flask under the magnetic stirring and ice-water bath, and was reacted for 1 h. The product, sulfur trioxide pyridine complex, was obtained.

Afterwards, 10.0 g of CS was added into this mixture under magnetic stirring. The reaction was sustained for 4 h at 45 °C. Then the resultant of reaction was precipitated by alcohol. The filter residue was washed three times with alcohol and a little of distilled water to remove the remaining pyridine, sulfuric acid and byproducts, respectively. The product SCS was dried. The process of sulfonation is depicted in Fig. 3(e). The degree of sulfonation substitution (DS) of SCS was measured by the barium sulfate-glutin nephelometery method using UV–vis spectrophotometer (model UV 2300, Tian Mei Co., China). The DS was defined as the number of substituted hydroxyl groups per AGU in the starch molecule, and the maximum value of DS is 3.0 (Cui et al., 2009). The DS of SCS was measured as 2.20.

2.3. Preparation of SCS/PAA/PHR

The SCS/PAA/PHR was prepared by solution polymerization. At first, 1.67 g of SCS was dissolved in 35 mL of distilled water mixing with 3.0 g of PHR, then was added to 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. During this process, the PHR can be availably suspended, dispersed and coated by the SCS. Then, 10.0 g of AA was partially neutralized with KOH solution (4.67 g of KOH was dissolved in 25 mL of distilled water), and 1.7 wt.% KPS (related to AA) and 0.3 wt.% NMBA (related to AA) were added to the partly neutralized AA solution. The AA solution was added to the SCS/PHR mixture solution described above under the magnetic stirring. The oil bath was heated slowly to 75 °C and incubated for 3 h to complete the polymerization. Then the resulting product was dried at 100 °C to a constant weight, and the dried product was milled to 20 mesh for further use.

2.4. Characterizations

The CS, SCS/PHR, SCS/PAA/PHR and PHR were characterized by Fourier Transform Infrared Spectroscopy (FTIR) analysis. The performance was carried out on a Nicolet 6700FT-IR (Thermo Nicolet, USA).

X-ray photoelectron spectroscopy (XPS) was employed to investigate the composition of SCS/PAA and SCS/PAA/PHR. The spectra were recorded on an ESCALAB 250 of Thermo Fisher Scientific

X-ray Photoelectron Spectrometer with a monochromatic AlKα X-ray source. The C 1s high-resolution analysis and low-resolution with a scan width of 20 eV, were conducted.

2.5. Measurement of water absorbency of the SCS/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 from water, while the residual water was wiped up with filter paper, and weighed the bag. The water absorbency Q_{eq} (H_2O) of the SAP was calculated using Eq. (1):

$$Q_{eq}(H_2O) = \frac{m_2 - m_1 - m_0}{m_1} \tag{1}$$

where m_0, m_1 and m_2 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 available phosphorus content in SCS/PAA/PHR

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

2.7. Measurement of water-soluble phosphorus and water soluble potassium content in SCS/PAA/PHR

The water-soluble phosphorus content in SCS/PAA/PHR was measured by colorimetric analysis (Lu, 1999). Phosphorus reacted with ammonium molybdate and potassium antimonyl tartrate to form a molybdophosphate in acid solution. Then, the molybdophosphate was reduced by ascorbic acid to form a blue complex (phosphomolybdenum blue). In the first step, phosphorus reacted with ammonium molybdate to form a molybdophosphate in acid solution ($7PO_4^{3-} + 21NH_4^+ + 12Mo_7O_{24}^{6-} + 72H^+ = 7(NH_4)_3[PMo_{12}O_{40}]\downarrow + 36H_2O$). In the second step, the molybdophosphate was reduced by ascorbic acid to form a blue complex (phosphomolybdenum blue) in the presence of oxygen potassium antimonyl tartrate ($(NH_4)_3[PMo_{12}O_{40}] \rightarrow H_3PO_4{\cdot}2Mo_2O_5 + H_3PO_4{\cdot}10MoO_3{\cdot}2Mo_2O_5$). The oxygenpotassium antimonyl tartrate did not participate in the colour reaction, but it played an important role in sheltering the interference elements such as Si and Fe. The colour depth of the complex was proportional to the consistence of phosphate, and the absorbance can be 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 SAP was measured by flame photometry (model 6400A, Shanghai Precision and Scientific Instrument Co. Ltd., China) (Lu, 1999).

2.8. Sustained release behaviours of the SCS/PAA/PHR

0.2 g of dry SCS/PAA/PHR and 0.2 g of PHR were added to a 500 mL of flask containing 250 mL distilled water (release medium), respectively, to study the release behaviours of P and K. Then, the flasks were put into an incubator, and the temperature was set at 25 °C. After a period of time (2 h, 4 h, 6 h, 8 h, 24 h, 48 h, 96 h, 168 h, 360 h and 720 h), 25 mL of extracted fluid was sampled for P and K measurement, then 25 mL of distilled water was added into the flasks to maintain a constant amount of solvent. The P and K content were measured by colorimetric analysis and flame photometry, respectively (Lu, 1999). The release ratios of phosphorus (P%) and potassium (K%) were calculated by the following equation:

$$P\% = \frac{m_1}{m_0} \times 100$$

$$K\% = \frac{m_3}{m_2} \times 100$$

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

3. Results and discussion

3.1. XPS analysis

The XPS study of SCS/PAA and SCS/PAA/PHR was investigated. As Fig. S1 shown, new peaks133.20 eV and 347.73 eV which are attributed to element P and Ca that phosphate rock contains, present in the wide scan XPS spectrum of SCS/PAA/PHR, which suggests that phosphate rock is loaded in SCS/PAA.

Fig. 1(a) and (b) shows the S 2p spectra of samples. There are two separate peaks at 169.58 and 168.43 eV which are ascribable to the double S $2p_{3/2,\,1/2}$ of $-SO_3^-$ group of SCS/PAA. After loading PHR, these two separate peaks are at 169.91 eV and at 168.72 eV, respectively, which slightly move to higher binding energy (BE). This change reveals that the calcium phosphate compounds in PHR, such as $Ca_3(PO_4)_2$ and $CaHPO_4$, bond to the sulfonate groups of SCS, because that the covalent bond between calcium and sulfur atom is formed by accepting long pair of electrons from the sulfur atom, and this covalent bond decreases the electron cloud density of sulfur atom. In other word, the electron-withdrawing group augments the BE of the electrons of core level, thus results in this change (Jin & Bai, 2002; Park, Yun, & Park, 2008). Additionally, considering the change of BE is weak, the covalent bond might be slight due to the fact that during process of polymerization of SCS/PAA/PHR, the covalent bond between calcium and sulfur is undermined.

Fig. 1(c) and (d) displays the C 1s spectra of samples. The peaks of SCS/PAA at 284.81, 285.45 and 288.47 eV correspond to the carbon atom in the forms of $C{-}C$, $C{-}O$ and $C{=}O$, respectively. It can be observed that the peaks of $C{-}O$ and $C{=}O$ which are belonged to $-COO^-$ of SCS shift to lower BE slightly after loading PHR. Additionally, as Table S1 shown, the alteration value of related content of $C{-}O$ (24.00–17.71%) is smaller than that of $C{=}O$ (12.12–21.82%), indicating that the tendency of free phosphorus and calcium, as well as the calcium phosphate compounds which bond to $C{=}O$, is stronger than that to $C{-}O$. This may ascribe to the fact that during the polymerization the content of SCS is much smaller than that of AA in SCS/PAA/PHR. Though the electron-withdrawing ability of $-SO_3^-$ is stronger than that of $-COO^-$, the content of SCS in SCS/PAA/PHR is too small, and the amount of $-SO_3^-$ is smaller than that of $-COO^-$, so the free phosphorus and calcium and the calcium phosphate compounds tend to bond to $C{=}O$.

As Fig. 1(e) and (f) depicted, both O 1s spectra of SCS/PAA before and after loading PHR contain two peaks which are assigned to $C{=}O$ (around 531 eV) and $C{-}O$ (around 533 eV). It is obvious that the both of them shift to lower BE ($C{=}O$: 531.76–531.64 eV; $C{-}O$: 533.37–533.03 eV), and the related content of $C{-}O$ (14.93%) increases to 41.71% while related content $C{=}O$ (85.07%) declines to

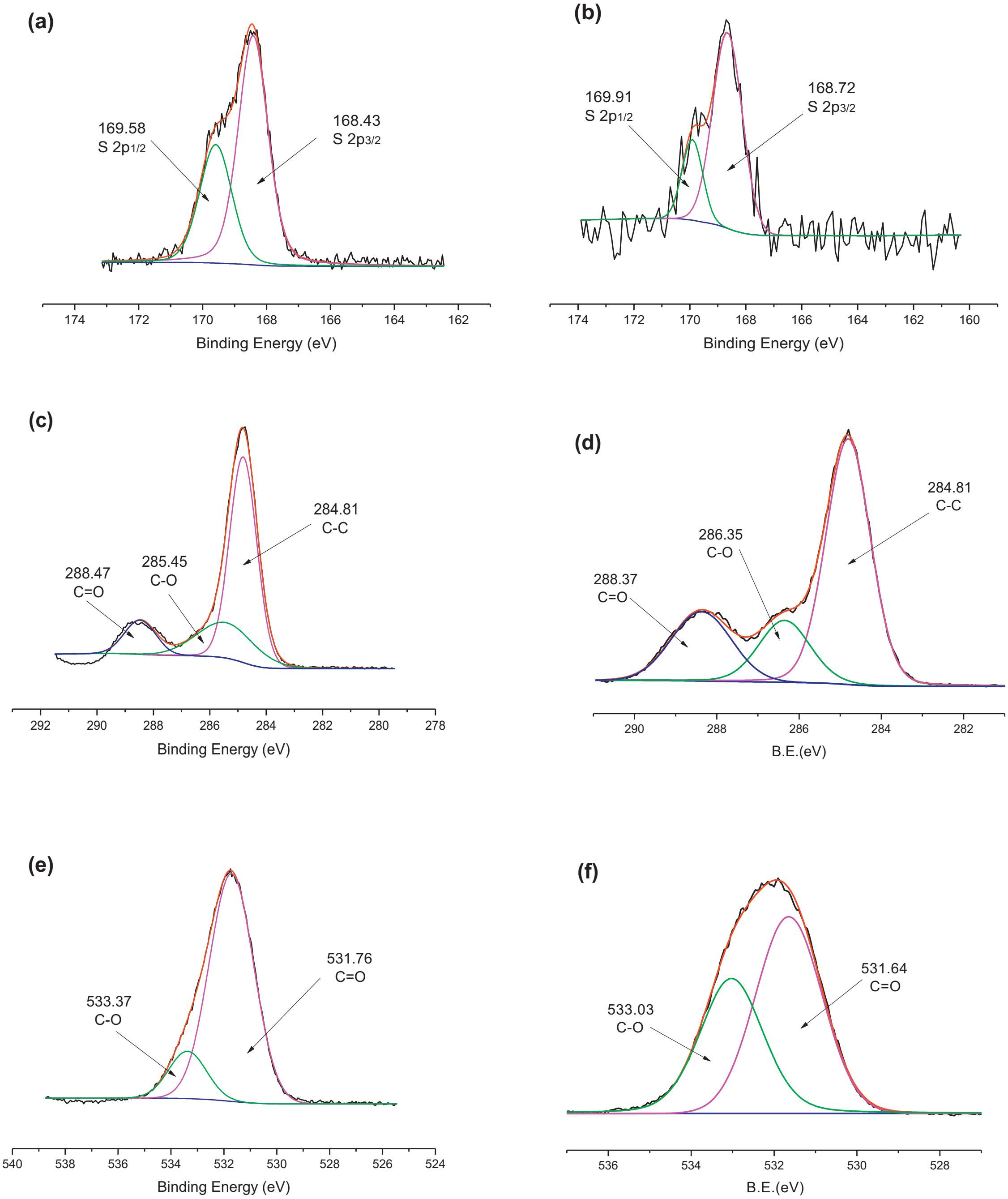

Fig. 1. The XPS spectra of: (a) S 2p of SCS/PAA; (b) S 2p of SCS/PAA/PHR; (c) C 1s of SCS/PAA; (d) C 1s of SCS/PAA/PHR; (e) O 1s of SCS/PAA/PHR; (f) O 1s of SCS/PAA.

58.29%, which also suggests that the free phosphorus and calcium, and calcium phosphate compounds bond to the–COO$^-$, resulting in the fact that the electron density towards the oxygen atoms is decreased (Liu et al., 2011).

These results reveal that the both —SO$_3$$^-$ and —COO$^-$ are involved in the bond with the phosphate rock, while the tendency to bond to —SO$_3$$^-$ is stronger than that to —COO$^-$. Thus, the phosphate rock can be suspended and stabled well to embed into the cross-linking network of the copolymer.

3.2. FTIR analysis

The FTIR spectra of corn starch (CS), sulfonated corn starch (SCS), SCS/PHR, SCS/PAA/PHR, and PHR are shown in Fig. 2. In the FTIR spectrum of CS (Fig. 2(a)), the absorption band at 3436 cm^{-1} ascribes to the —OH stretching vibration of the glucose unit, and the absorption bands at 1010 cm^{-1}, 1079 cm^{-1} and 1156 cm^{-1} are attributed to C—O stretching vibration of the glucose unit. Additionally, the absorption bands at 1376 cm^{-1} and 1460 cm^{-1} belong to O—H in-plane bending vibration of the glucose unit. Fig. 2(b) displays the FTIR spectrum of SCS, compared with Fig. 2(a), the new absorption bands appeared at 1541 cm^{-1} and 1224 cm^{-1}are ascribed to the asymmetric and symmetric stretching vibration of —SO$_2$—, respectively, while, the new peak at 816 cm^{-1} belongs to the symmetrical C—O—S stretching vibration, which indicates that the CS is sulfated successfully. Fig. 2(d) is the FTIR spectrum of SCS/PAA/PHR, by comparing with the spectra of SCS (Fig. 2(b)) and SCS/PHR (Fig. 2(c)), the polymerization of AA is

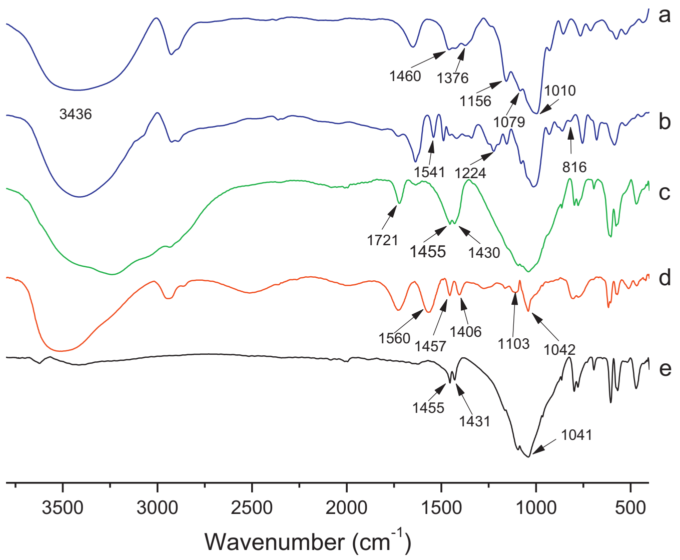

Fig. 2. The FTIR spectra of (a) CS; (b) SCS; (c) SCS/PHR; (d) SCS/PAA/PHR; (e) PHR.

confirmed by the appearance of absorption bands at 1560 cm^{-1} (asymmetrical stretching vibration of COO$^-$) and 1406 cm^{-1} (symmetrical stretching vibration of COO$^-$). In addition, the absorption bands at 1103 cm^{-1} and 1042 cm^{-1} in spectrum of SCS/PAA/PHR can be ascribed to PO_4^{3-} stretching vibration of the PHR, while these two peaks and the peak at 1224 cm^{-1} (symmetric stretching vibration of $-SO_2-$) are overlapped in that of SCS/PHR. It can be observed that the intensity of peak at 1224 cm^{-1} in SCS/PAA/PHR is very weak. All these suggest that PHR is bound by the polymer successfully (Abd El-Rehim & Diaa, 2012; Xing, Zhang, Ju, & Yang, 2006).

3.3. *The function of sulfonated corn starch in the cross-linking process of polymers*

As Fig. 3(a) and (b) shown, after depositing for 3 h, the sediment of PHR is observed in the bottle mixing with AA solution, while there is no sediment in the one mixing with SCS and AA solution. The result indicates that SCS is capable to suspend and dispersed the phosphate rock well comparing with the AA solution.

Fig. 3(c) and (d) displays the photograph that SAP based on different type of polymers embedding PHR. It is obvious that the bottom of one based on only PAA mixing with CS and embedding PHR has a thin layer of brown PHR sediment, however, the bottom of one containing SCS does not. This attributes to the fact that the PHR can be suspended and well-dispersed with SCS solution during the cross-linking process of copolymers, because that the electron-withdrawing ability of $-SO_3^-$ is strong to firm the covalent bond to phosphorus and calcium, as well as the calcium phosphate compounds. Moreover, since the amount of phosphate rock is small and some of them might bond to the small amount of PAA, the thick layer of brown phosphate rock sediment is hardly viewed in Fig. 3(a).

3.4. *Impacts on the water absorbency*

The effect of content of crosslinker (related to AA) on the water absorbency is shown in Fig. 4(a). The water absorbency increases with the augment of crosslinker content from 0.05 wt.% (weight percent) to 0.3 wt.%, but declines with excess crosslinker content. Clearly, the water absorbency is related to the crosslinking density of the polymeric network (Flory, 1953). When the content of crosslinker is below 0.3 wt.%, the SAP polymeric network cannot be formed efficiently due to the absence of adequate crosslink points, resulting in semi-soluble SAP and low water adsorption capacity. When the content of crosslinker is more than 0.3 wt.%, the crosslinking density is increased with the augment of content of crosslinker, and the network space gets compact, bringing about the decline of water absorbency. Similar observation was reported by Li, Wang, and Chen (2004) and Chen and Zhao (1999).

The feed ratio of initiator impacts significantly on the polymerization process. It can be observed in Fig. 4(b) that the maximum water absorbency is obtained at 1.7 wt.% initiator content (related to AA). However, a further augment or decrease of initiator content generates the decline of water absorbency. The reason might be that the most of initiator is consumed in producing a large number of growing polymer chain when the initiator content is low (Athawate & Lele, 2000). Therefore, the polymerization yield and the water adsorption capacity of the SCS/PAA/PHR rises with the increase of initiator content when it is low than 1.7 wt.%. However, when initiator content exceeds 1.7 wt.%, the plethoric free-radicals appears, resulting in popcorn polymerization and terminating steps due to the fact that the heat accumulation originated from fast polymerization, accompanying with low molecular weight SAP and weak water absorption capacity (Allcock & Frederick, 1981).

Water absorption capacity of the SCS/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. 5, the maximum water absorbency of SCS/PAA/PHR (498 g g^{-1} (water/SAP) in distilled water and 65 g g^{-1} in 0.9 wt.% NaCl solution) is obtained when the neutralization present of PAA is 60%, but when the neutralization present of PAA is over 60%, the water absorption capacity declines. This is attributed to the fact that the liquid absorbency is affected by the osmotic pressure difference. When the neutralization percent of AA increases from 50% to 60%, the amount of K^+ ions rises, which leads to 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 over 60%, SCS/PAA/PHR tends to become water-soluble, resulting in the decrease of water absorption capacity (Liu, Miao, Wang, & Yin, 2009).

The impact of distilled water content (related to AA) on the water absorbency was investigated by changing the total water weight percent in polymerization. Fig. 6 depicts that the maximum water absorbency is achieved when distilled water content is 600 wt.%, but when distilled water content is higher or lower than 600 wt.%, the water absorption capacity declines. This is because that the less water content causes a high density of AA, NMBA and KPS, resulting in excessive intense polymerization and crowded close-knit polymeric network, which causes the decrease 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 ratio is over 600 wt.%. As a result, the copolymerization cannot be finished fully and the product is semiliquid, bringing about a serious decline of water absorption capacity.

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

The impact of PHR content ratio (weight percent related to AA) on the water absorption capacity was conducted, which reveals that the water absorption capacity of the SCS/PAA/PHR decreases with the rising PHR content (Table 1). This phenomenon can be explained as follows: since water soluble phosphate in PHR will form positive ions Ca^{2+} and negative ions PO_4^{3-} via ionization, Ca^{2+} will chelate the negative charged $-COO^-$ of the poly (acrylic acid) network and reduce their water affinity, which will decrease the osmotic pressure difference and bring about lower water absorption capacity. Moreover, when the PHR content is excessive, the excess amount

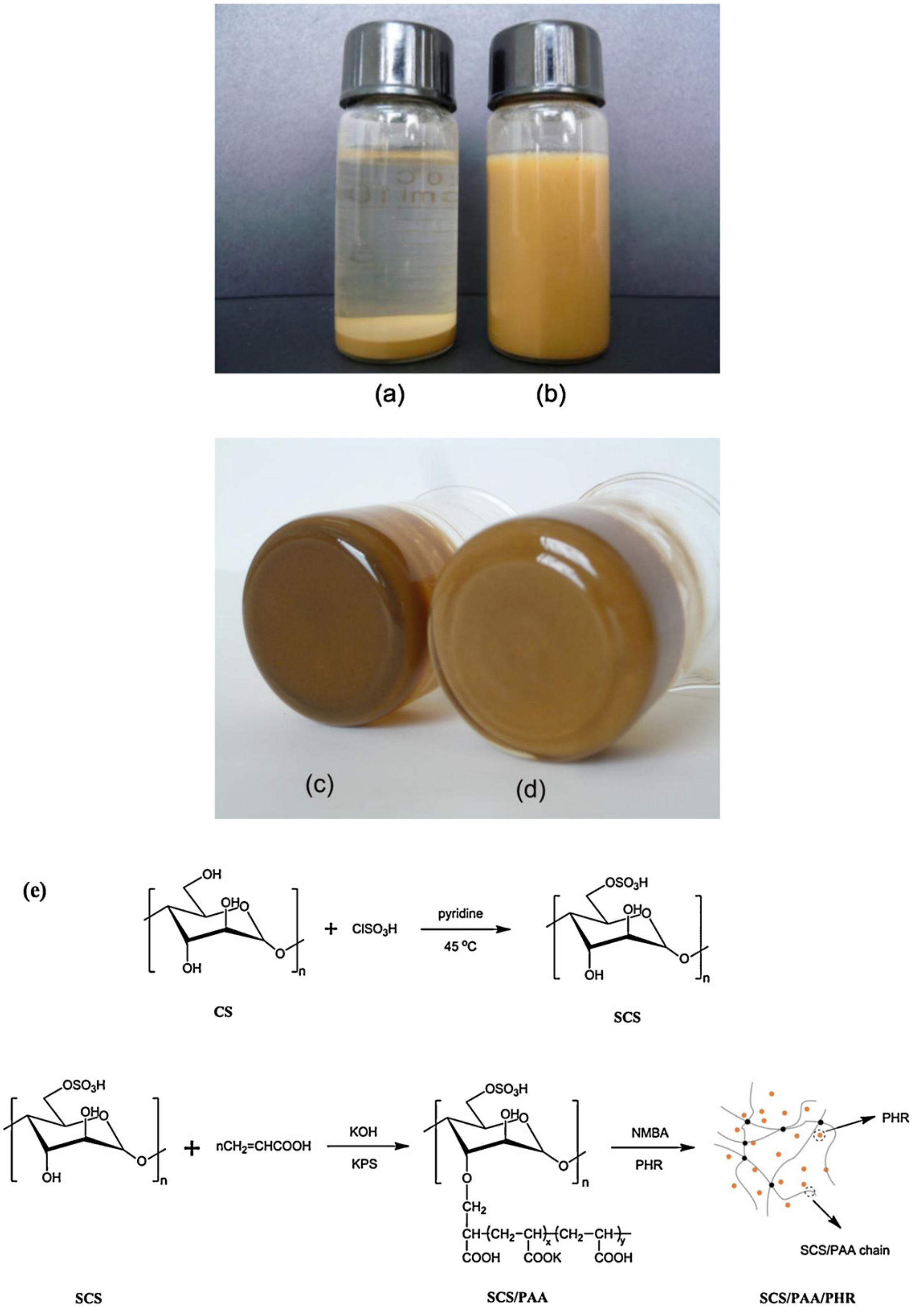

Fig. 3. (a) Phosphate rock mixed with AA solution after 3 h; (b) phosphate rock mixed with SCS and AA solution after 3 h; (c) SAP based on CS/PAA/PHR; (d) SAP based on SCS/PAA/PHR; (e) synthesis of SCS, and the structural formulae of copolymers.

Table 1
Effect of PHR content on available phosphorus, water-soluble phosphorus content and water absorbency. $T = 75\,^{\circ}C$, KPS = 1.7 wt.%, NMBA = 0.3 wt.%, SCS = 1.67 g, AA = 10 g, KOH = 4.67 g.

PHR content[a]	Total phosphorus[b] ($mg\,kg^{-1}$)	Available phosphorus[c] ($mg\,kg^{-1}$)	Water-soluble phosphorus[d] ($mg\,kg^{-1}$)	Q_{eq}[e] ($g\,g^{-1}$)	Q_{eq}[f] ($g\,g^{-1}$)
10%	13,086	2858	11.43	498	65
20%	24,757	5406	21.62	392	58
30%	35,230	7592	29.77	359	54
40%	44,680	9355	37.02	336	45
50%	53,260	10,828	42.51	275	37

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

of PHR cannot be enwrapped efficiently by CSC/PAA, and congests in the void or inter-space of polymeric network, which will hinder water pervasion and lead to the decline of water absorption capacity.

3.6. Available phosphorus and water-soluble phosphorus content in SCS/PAA/PHR, and the sustained release behaviours of water soluble potassium

The amount of available phosphorus and water-soluble phosphorus in SCS/PAA/PHR are exhibited in Table 1. Both of them increase with the augment of the feed PHR content. However, the growth rate of available phosphorus and water-soluble phosphorus amount is much lower than that of the feed PHR content. This maybe because that in the process of polymerization when the amount of PHR exceeds the maximum that the SCS can stabilize and suspend the PHR, the excessive amount of PHR cannot be suspended and stabilized effectively by SCS, resulting in a mass of deposit in the polymerization solution. Consequently, the filled PHR content in the SCS/PAA/PHR is lower than the presupposed PHR content.

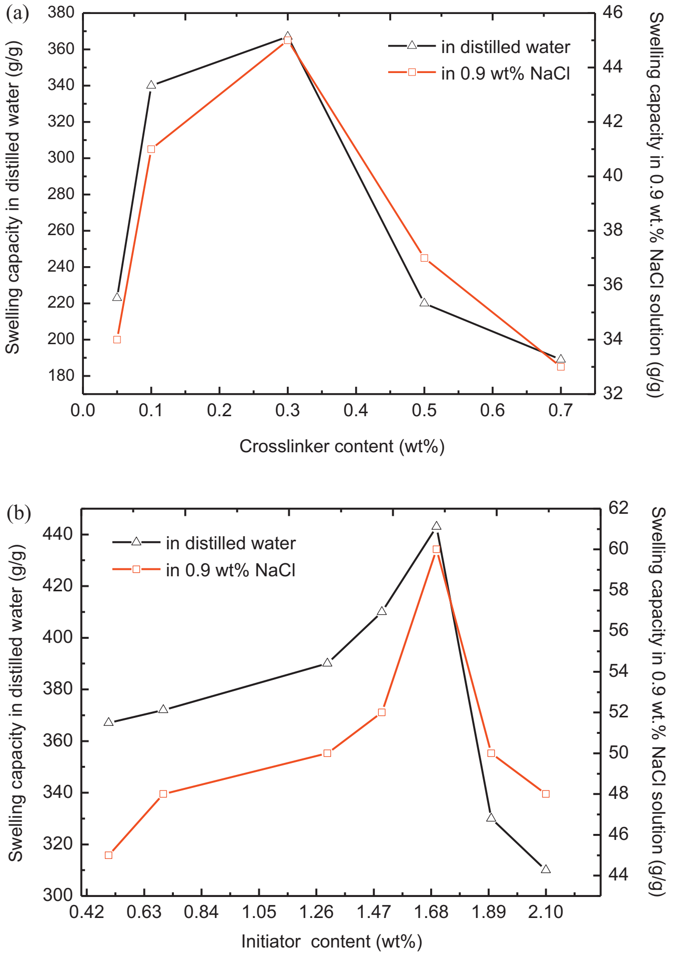

Fig. 4. (a) Effect of crosslinker content on the water absorbency. $T = 75\,^{\circ}C$, KPS = 0.5 wt.%, SCS = 1.67 g, AA = 10 g, PHR = 1 g, KOH = 5.44 g; (b) effect of initiator content on the water absorbency. $T = 75\,^{\circ}C$, NMBA = 0.3 wt.%, SCS = 1.67 g, AA = 10 g, PHR = 1 g, KOH = 5.44 g.

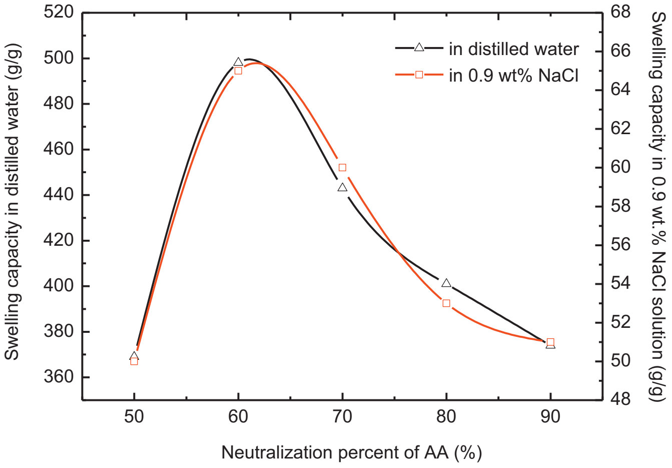

Fig. 5. Effect of the neutralization percent of AA on the water absorbency. $T = 75\,^{\circ}C$, KPS = 1.7 wt.%, NMBA = 0.3 wt.%, SCS = 1.67 g, AA = 10 g, PHR = 1 g.

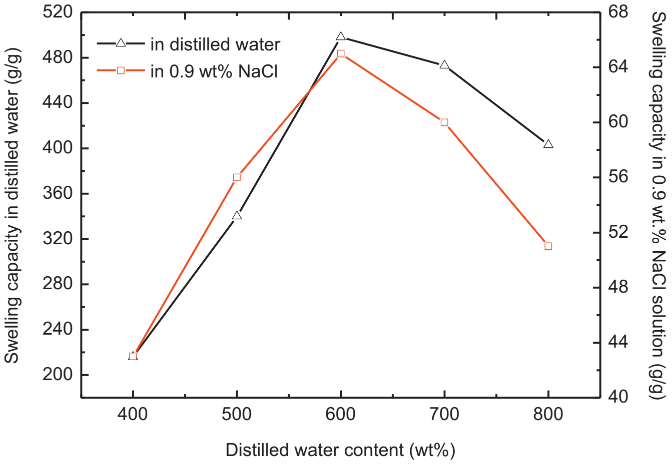

Fig. 6. Effect of distilled water content on the water absorbency. $T = 75\,^{\circ}C$, KPS = 1.7 wt.%, NMBA = 0.3 wt.%, SCS = 1.67 g, AA = 10 g, PHR = 1 g, KOH = 4.67 g.

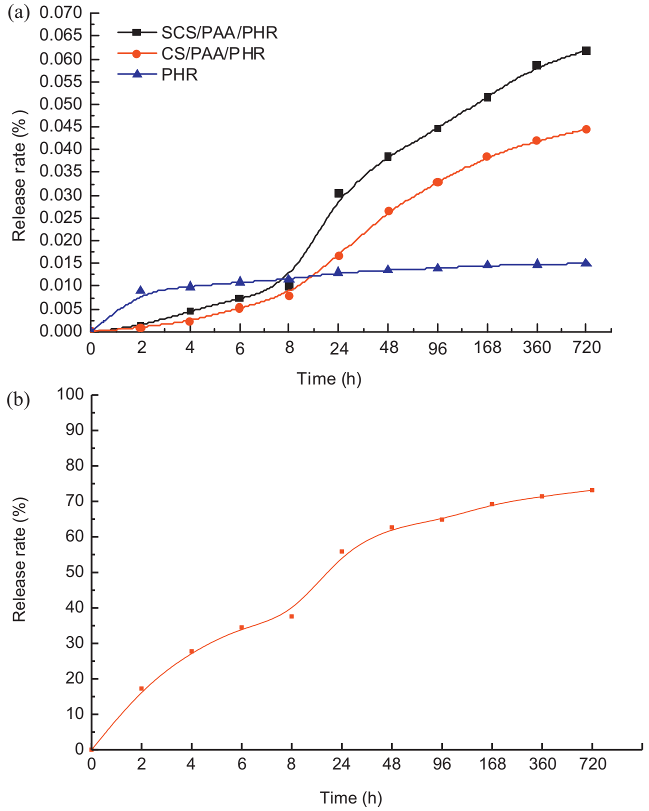

Fig. 7. (a) Comparison of the phosphorus release between PHR, CS/PAA/PHR and poly SCS/PAA/PHR, SCS (CS) = 1.67 g, PHR = 3 g; (b) the release behaviours of water soluble potassium, KOH = 4.67 g.

As Table 1 shown, when the PHR content in prepared SAP is higher than 30 wt.%, the water absorbency in distilled water and water absorbency in 0.9% NaCl solution are relatively lower, but the total phosphorus is much higher than the prepared SAP which the PHR content is lower 30 wt.%. However, when the PHR content in prepared SAP is higher than 30 wt.%, the water absorbency in distilled water and water absorbency in 0.9% NaCl solution is relatively higher, but the total phosphorus is much lower than the prepared SAP. Thus, considering the comprehensive advantage of water absorbency, available phosphorus and water-soluble phosphorus content, 30 wt.% of PHR (weight percent to AA) is 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 are 1.7 wt.%, 0.3 wt.%, 30 wt.%, 600 wt.% and 60%, respectively. The water absorbency of SCS/PAA/PHR in distilled water and 0.9 wt.% NaCl solution are 359 g g^{-1} and 54 g g^{-1} respectively, while the available phosphorus and water-soluble phosphorus content of the SCS/PAA/PHR are 7592 mg kg^{-1} and 29.77 mg kg^{-1}, respectively.

Fig. 7(a) displays the release behaviours of water-soluble phosphorus in PHR, CS/PAA/PHR and SCS/PAA/PHR. It is well known that water-soluble phosphorus can be dissolved in water easily, so an initially high release rate followed by a rapidly declining release rate, and more than 90% of water-soluble phosphorus in PHR is released within 4 h. Moreover, the released phosphorus in PHR only originates from the soluble part of the PHR, and the insoluble part cannot be released, thus 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 CS/PAA/PHR and SCS/PAA/PHR, the water-soluble phosphorus shows a preferable sustained-release property. Moreover, the release ratios of phosphorus in CS/PAA/PHR and SCS/PAA/PHR are much higher than that of PHR after 24 h. The reason may be that some of the insoluble PHR is dissolved by the acidic microenvironment in the swollen hydrogel. After 30 days, the release ratio of phosphorus in SCS/PAA/PHR increases by about 40% and 350% over the CS/PAA/PHR and PHR, respectively. The discrepancy implies that SCS could greatly improve the amount of the released phosphorus. Being a kind of starch derivatives bearing sulfonate group, SCS can form a high viscosity in solution, suspend and disperse PHR in reaction solution well, then reduce the deposit amount of PHR during the polymerization. Moreover, the SCS/PAA/PHR can release much more water-soluble phosphorus by virtue of the dissolving erosion of PHR by SCS. In general, the total phosphorus/PHR: 22.9%; the available phosphorus/total phosphorus: 5%; water-soluble phosphorus/PHR: 25 mg kg^{-1}, 0.0025%; water-soluble phosphorus/total phosphorus: 0.014%. Due to the acid of SCS, a part of citric acid soluble phosphorus (the main content of water-insoluble phosphorus) transforms into water-soluble phosphorus, and is released. In our previous study, the amount of water-soluble phosphorus released from MSB/PAA/PHR is about 0.058% after 15 days (Zhong et al., 2012). However, the amount of water-soluble phosphorus released from SCS/PAA/PHR is over 0.060% after 15 days. These results indicate that the amount of phosphorus release is greatly improved by SCS. Although, the amount of release of water-soluble phosphorus after 30 days just reaches 0.065% of total phosphorus, which is about 4.5 times higher than that in pure PHR (only 0.014% of total phosphorus). This promoted-release (or be called as controlled-release) method of phosphorus has significant benefits for fertilizer delivery, and has valuable practicality in agriculture. Since the release of water-soluble phosphorus in SAP is a long-term process which will last for several years (SAP can be used about 5 years), moreover, humic in soil, vast organic-acid secreted by roots of plants, and some kinds of bacterial and enzyme in soil can also further decompose PHR, as a result, more amount of citric acid soluble phosphorus will transform into water-soluble phosphorus, and can be used as nutrient by plants.

Recently, the essential process is to render PHR into water-soluble phosphate to produce traditional phosphate fertilizer in phosphate fertilizer factory, and this process always consumes a great deal of acid and brings a great amount of waste acid water and waste gas HF. However, this study offers a new way to utilize the water-soluble phosphorus from PHR to feed crops phosphorus. Furthermore, this way 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.

Fig. 7(b) depicts the release behaviours of water soluble potassium in SCS/PAA/PHR. Comparing with water-soluble phosphorus in Fig. 7(a), both P and K show a sustained release property in 30 days. Obviously, the release rate of K is much faster than that of P in the early period. The discrepancy could be explained as follows: The released K originates from the water soluble K^+ ions which are mainly adsorbed by carboxyl groups and sulfonic groups of the polymeric network through electrostatic interaction, and the K^+ ions could be easily ionized in water and released out. At the beginning of the release period, the K release rate is very fast due to the high concentration difference between the SCS/PAA/PHR and the outside water. Subsequently, the release rate decreases as the amount of the K^+ ions is exhausted. For the release of phosphorus, the main component of the PHR is insoluble phosphates, but the water-soluble phosphorus content is very low. During the first 48 h, most of the water-soluble phosphorus is released by the dynamic exchange between the free water in SCS/PAA/PHR and the water outside. Then, the release rate of water-soluble phosphorus decreases but still keeps a higher release rate. This could be ascribable to the fact that some of the insoluble phosphate in PHR is dissolved to become water soluble phosphorus by the corrosion of SCS. This result indicates that in the SCS/PAA/PHR, the sustained release capability of phosphorus is much better than that of water soluble potassium. An analogy could be drawn that water insoluble PHR is more suitable to combine with SCS/PAA to prepare long term sustaining release fertilizer than other water-soluble commercial fertilizers.

Recently, only a few sustained fertilizers is not prepared as water-avoiding or waterproof types, including plastic (resin) embedding kinds, waterproof film coating kinds, corroding water-insoluble materials filled types, etc. Whereas, in this paper, our study suggests that it is not necessary to isolate fertilizers from water to avoid the loss of nutrient; on the contrary, fertilizers should combine with water, since fertilizers embedded in the SAP are not prone to lose due to the retention of adsorbed water by SAP. Even in case of rainstorm, SAP embedding fertilizers are soaked by flood temporarily, the nutrient loss rate is not egregious due to its trait of sustained release. Because when the water adsorption of SAP comes to saturation, the water pervasion reaches a balance, and the exudation and diffusion of nutrients accompanied by water out of the SAP will be slow. However, the exposed ordinary fertilizers might will be total lost in such a case. For the plastic film coated fertilizers, they have little nutrient loss under these circumstances, however, its nutrient cannot be absorbed by crops in the absence of water; likewise, the ordinary independent SAP is not beneficial to crops during long term drought season, because the only water supply without nutrients feeding is not barely enough for crops to combat drought efficiently. Therefore, the sustained fertilizers that combine with SAP and dismiss segregation from water are ideal. Besides, this way can reduce the use of traditional phosphate fertilizer and a great deal of acid waste in traditional phosphate fertilizer industry. It can reduce the pollution caused by traditional phosphate fertilizer industry to some extent.

4. Conclusions

In this article, an agricultural superabsorbent polymer based on sulfonated corn starch/poly (acrylic acid) embedding PHR was prepared to integrate water and fertilizers, and the integrating function of water and fertilizer supply was studied. The SCS can suspend and disperse the PHR well, and help the citric acid soluble phosphorus in PHR transform into water-soluble phosphorus, thus improve the amount of phosphorus release greatly. The water absorption capacity of the SCS/PAA/PHR was influenced by the content ratios of KPS, NMBA, PHR, distilled water and neutralization percent of AA. Both P and K were found to have excellent sustained release property, and the SCS/PAA could improve the release of P greatly. The results revealed that the system had several significant advantages over the conventional slow release fertilizers and agricultural SAP. Therefore, this combining system with good sustained fertilizers release and excellent water-retention is potentially useful in the crop cultivation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.10.030.

References

Abd El-Rehim, H. A., & Diaa, D. A. (2012). Radiation-induced eco-compatible sulfonated starch/acrylic acid graft copolymers for sucrose hydrolysis. *Carbohydrate Polymers*, *87*, 1905–1912.

Allcock, H. R., & Frederick, W. L. (1981). *Contemporary polymer chemistry*. Englewood Cliffs, NJ: Prentice Hall.

Al-Zahrani, S. M. (2000). Utilization of polyethylene and paraffin waxes as controlled delivery systems for different fertilizers. *Industrial & Engineering Chemistry Research*, *39*, 367–371.

Athawate, V. D., & Lele, V. (2000). Factors influencing absorbent properties of saponified starch-g-(acrylic acid-co-acrylamide). *Journal of Applied Polymer Science*, *77*, 2480–2485.

Biswas, D. R., & Narayanasamy, G. (1998). Direct and residual effectiveness of partially acidulated phosphate rocks as P fertilizer in a cowpea-wheat cropping sequence. *Journal of the Indian Society of Soil Science*, *46*, 406–412.

Chandra, P. K., Ghosh, K., & Varadachari, C. (2009). A new slow-releasing iron fertilizer. *Chemical Engineering Journal*, *155*, 451–456.

Chen, J., & Zhao, Y. (1999). An efficient preparation method for superabsorbent polymers. *Journal of Applied Polymer Science*, *74*, 119–124.

Cui, D., Liu, M., Wu, L., & Bi, Y. (2009). Synthesis of potato starch sulfate and optimization of the reaction conditions. *International Journal of Biological Macromolecules*, *44*, 294–299.

Flory, P. J. (1953). *Principles of polymer chemistry*. Ithaca, New York: Cornell University Press.

Jarosiewicz, A., & Tomaszewska, M. (2003). Controlled-release NPK fertilizer encapsulated by polymeric membranes. *Journal of Agricultural and Food Chemistry*, *51*, 413–417.

Jin, L., & Bai, R. (2002). Mechanisms of lead adsorption on chitosan/PVA hydrogel beads. *Langmuir*, *18*, 9765–9770.

Liang, R., Yuan, H., Xi, G., & Zhou, Q. (2009). Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it. *Carbohydrate Polymers*, *77*, 181–187.

Li, A., Wang, A., & Chen, J. (2004). Studies on poly(acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization. *Journal of Applied Polymer Science*, *92*, 1596–1603.

Lim, D. W., Wang, H. S., Yoon, K. J., & Ko, S. W. (2001). Synthesis and absorbency of a superabsorbent from sodium starch sulfate-g-polyacrylonitrile. *Journal of Applied Polymer Science*, *79*, 1423–1430.

Liu, H., Yang, F., Zheng, Y., Kang, J., Qu, J., & Chen, J. P. (2011). Improvement of metal adsorption onto chitosan/*Sargassum* sp. composite sorbent by an innovative ion-imprint technology. *Water Research*, *45*, 145–154.

Liu, Z., Miao, Y., Wang, Z., & Yin, G. (2009). Synthesis and characterization of a novel super-absorbent based on chemically modified pulverized wheat straw and acrylic acid. *Carbohydrate Polymers*, *77*, 131–135.

Lu, R. K. (1999). *Analysis method of soil agro-chemistry*. Beijing: China Agricultural Technology Press.

Marcì, G., Mele, G., Palmisano, L., Pulito, P., & Sannino, A. (2006). Environmentally sustainable production of cellulose-based superabsorbent hydrogels. *Green Chemistry*, *8*, 439–444.

Mathews, A. S., & Narine, S. (2010). Poly[N-isopropyl acrylamide]-co-polyurethane copolymers for controlled release of urea. *Journal of Polymer Science Part A: Polymer Chemistry*, *48*, 3236–3243.

Menon, R. G., & Chien, S. H. (1996). *Compaction of phosphate rocks with soluble phosphates*. Muscle Shoals, Alabama, USA: International Fertilizer Development Center.

Narayanasamy, G., & Biswas, D. R. (1998). Phosphate rocks of India: Potentialities and constraints. *Fertilizer News*, *43*, 21–28.

Ni, B., Liu, M., & Lü, S. (2009). Multifunctional slow-release urea fertilizer from ethyl cellulose and super absorbent coated formulations. *Chemical Engineering Journal*, *155*, 892–898.

Ni, B., Liu, M., Lü, S., Xie, L., & Wang, Y. (2011). Multifunctional slow-release organic–inorganic compound fertilizer. *Journal of Agricultural and Food Chemistry*, *59*, 10169–10175.

Nykänen, V. P. S., Nykänen, A., Puska, M. A., Goulart Silva, G., & Ruokolainen, J. (2011). Dual-responsive and super absorbing thermally cross-linked hydrogel based on methacrylate substituted polyphosphazene. *Soft Matter*, *7*, 4414–4424.

Omidian, H., Rocca, J. G., & Park, K. (2005). Advances in superporous hydrogels. *Journal of Controlled Release*, *102*, 3–12.

Park, D., Yun, Y. S., & Park, J. M. (2008). XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption. *Journal of Colloid and Interface Science*, *317*, 54–61.

Piao, S., Ciais, P., Huang, Y., Shen, Z., Peng, S., Li, J., et al. (2010). The impacts of climate change on water resources and agriculture in China. *Nature*, *467*, 43–51.

Prasad, R., Rajale, G. B., & Lakhdive, B. A. (1971). Nitrification retarders and slow-release nitrogen fertilizers. *Advances in Agronomy*, *23*, 337–383.

Ray, S. K., Varadachari, C., & Ghosh, K. (1993). Novel slow-releasing micronutrient fertilizers. 1. Zinc compounds. *Industrial & Engineering Chemistry Research*, *32*, 1218–1227.

Sengul, H., Ozer, A. K., & Sahin Gulaboglu, M. (2006). Beneficiation of Mardin-Mazıdaği (Turkey) calcareous phosphate rock using dilute acetic acid solutions. *Chemical Engineering Journal*, *122*, 135–140.

Teodorescu, M., Lungu, A., Stanescu, P. O., & Neamtu, C. (2009). Preparation and properties of novel slow-release NPK agrochemical formulations based on poly(acrylic acid) hydrogels and liquid fertilizers. *Industrial & Engineering Chemistry Research*, *48*, 6527–6534.

Tilman, D., Cassman, K. G., Matson, P. A., Naylor, R., & Polasky, S. (2002). Agricultural sustainability and intensive production practices. *Nature*, *418*, 671–677.

Vassilev, N., Vassileva, M., Fenice, M., & Federici, F. (2001). Immobilized cell technology applied in solubilization of insoluble inorganic (rock) phosphates and P plant acquisition. *Bioresource Technology*, *79*, 263–273.

Wang, W., & Wang, A. (2010). Nanocomposite of carboxymethyl cellulose and attapulgite as a novel pH-sensitive superabsorbent: Synthesis, characterization and properties. *Carbohydrate Polymers*, *82*, 83–91.

Wu, L., & Liu, M. (2008). Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention. *Carbohydrate Polymers*, *72*, 240–247.

Wu, L., Liu, M., & Liang, R. (2008). Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention. *Bioresource Technology*, *99*, 547–554.

Xing, G. X., Zhang, S. F., Ju, B. Z., & Yang, J. Z. (2006). Study on adsorption behavior of crosslinked cationic starch maleate for chromium(VI). *Carbohydrate Polymers*, *66*(2), 246–251.

Zhong, K., Zheng, X. L., Mao, X. Y., Lin, Z. T., & Jiang, G. B. (2012). Sugarcane bagasse derivative-based superabsorbent containing phosphate rock with water-fertilizer integration. *Carbohydrate Polymers*, *90*, 820–826.