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Synthesis, flocculation and adsorption performance of amphoteric starch

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ABSTRACT

A novel amphoteric copolymer flocculant was synthesized by incorporating a cationic moiety 2,3-epoxypropyl trimethyl ammonium chloride (GTA) and an anion moiety phosphate onto the backbone of starch with microwave radiation. The synthesized starch copolymer was characterized and examined by FTIR, ^{1}H NMR spectroscopy, scanning electron microscopy (SEM), molecular mass and polydispersity, swelling power and solubility index. Flocculation performance was evaluated in 50 mg/L methyl violet solution. It has been found that these flocculation characteristics mainly depended on the charge neutralization, followed by the interchain bridging of the amphoteric copolymer. Also, adsorption to Pb (II) solution was investigated by jar test. The results showed that the adsorption capacity of amphoteric copolymer correlated with pH value, adsorption time and initial Pb (II) concentration.

1. Introduction

Of all the synthetic and natural polymers utilized for the solid–liquid separation in this treatment process, starch derivatives used as flocculants to remove colloidal particles and heavy metals for flocculation have attracted considerable attention in recent years (Guo, Sun, Li, Liu, & Ji, 2009; Shogren, 2009; Xing, Zhang, Ju, & Yang, 2006a; Zhao et al., 2010; Zheng, Hua, & Wang, 2010). Various functional groups (amino, imino, sulphonium, phosphonium, etc.) have been incorporated in starch to obtain effective flocculants with good mineral binding properties to treat organic and inorganic matter in wastewater (Jarnstrom, Lason, & Rigdahl, 1995; Pal, Mal, & Singh, 2005; Singh & Tiwari, 2008). The modified polysaccharides are usually synthesized by conventional redox grafting method (da Silva, de Paula, & Feitosa, 2007; Gautam, Ranvijay, Ghosh, & Sagar, 2009; Guoren, Xiaoqin, Rufeng, Jing, & Shifang, 2011; Kaith, Singha, & Kalia, 2007; Kang, Cai, & Liu, 2006; Rumei, Bo, Yijiu, & Mingzhen, 2011; Singh, Tiwari, & Sanghi, 2005; Vittoria et al., 2011). Compared with the conventional methods, microwave radiation synthesis is becoming a standard technique applied in starch modification based on its advantages of energy saving, high conversion, and rapidity (Sumit, Ankita, Gautam, & Usha, 2011; Wei, Cheng, & Zheng, 2008; Xing, Zhang, Ju, & Yang, 2006b).

In previous studies of flocculated systems, it has been reiterated that adsorption and flocculation processes must occur simultaneously to work rather than act as separate mechanisms (Angle, Smith, & Wentzell, 1997; Khalil & Aly, 2004; Larsson & Wall, 1998; Sableviciene, Klimaviciute, Bendoraitiene, & Zemaitaitis, 2005). Moreover, the correlation between adsorption and flocculation and their kinetics were also investigated (Bratskaya, Schwarz, Liebert, & Heinze, 2005; Chen, Liu, & Wang, 2007; Nystrom, Backfolk, Rosenholm, & Nurmi, 2003). However, few attempts have been made to reveal the flocculation and adsorption mechanisms of cross-linked starch for colloidal particles and heavy metal ions simultaneously.

In this paper, amphoteric starch was synthesized in two copolymerization processes with microwave-assisted method and simultaneously studied its flocculation and adsorption ability. Also the effects of microwave power, microwave radiation time and reagent concentrations (GTA and phosphates) were evaluated. The aim of this work was to prepare the multifunctional material modified from the natural product in order to realize the efficient adsorption for heavy metal ion and the synchronal flocculation for organic colloids.

2. Materials and methods

2.1. Materials

Waxy maize starch with a moisture content of 13.4% was purchased from Changchun Dacheng Maize Starch Co., Ltd., PR China. GTA (2,3-epoxypropyl trimethyl ammonium chloride) was obtained from Shengli Oil Field Longyu Chemical Co., Ltd., PR China. The vacuum drying equipment (DJF-6050) produced by the Guangzhou Kangheng Instrument Co., Ltd., PR China was applied for vacuum dehydration. A Galanz (Model No. P70D20TL-D4) domestic microwave oven was used for the experiment.

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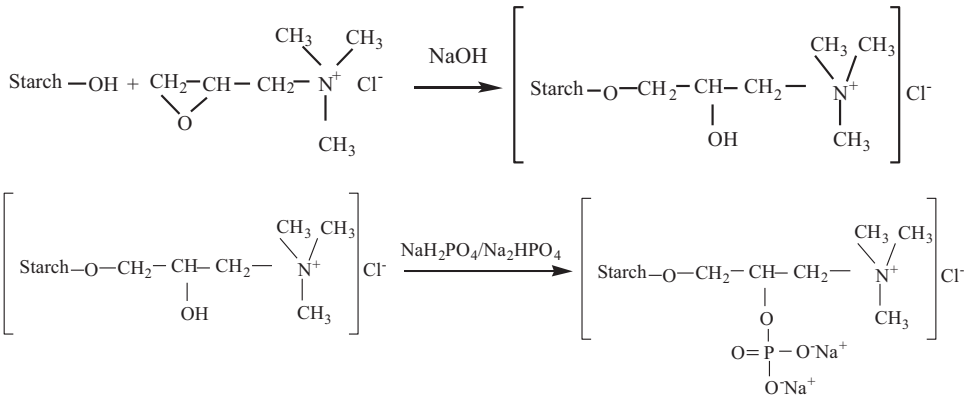

Scheme 1. Synthesis of amphoteric starch.

$NaH_2PO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}12H_2O$, sodium hydroxide, hydrochloric acid and ethanol were purchased from Guangzhou Chemical Reagent Factory PR China, and ammonium molybdate, methyl violet 2B, lead nitrate were purchased from Tianjin Damao Chemical Reagent Factory, PR China. All these reagents were of analytical grade and were applied directly. All solutions were prepared by deionized water.

2.2. Synthesis of amphoteric starch with microwave radiation

Typically, 1.50 g GTA (2,3-epoxypropyl trimethyl ammonium chloride) was added to the 100 mL vessel containing 5 mL sodium hydroxide (0.10 g/mL) aqueous. The solution was stirred thoroughly for 10 min. 10.00 g maize starch was added to above mixture. Stirring was continued for 0.5 h at a 70 °C water-bath for preheating, and then placed on the turntable of a microwave oven (Galanz P70D20TL-D4, PR China). Then, microwave irradiation was performed. Periodically, the microwave irradiation was paused just before boiling of the reaction mixture starts and this was done to prevent formation of vapors. This microwave irradiation-cooling cycle was repeated for 5 min, and its temperature reached 60 °C (1st min), 67 °C (2nd min),71 °C (3rd min),78 °C (4th min), 83 °C (5th min), respectively. Then the reaction vessel and its contents were finally cooled to room temperature. The precipitate left in the reaction vessel was collected and washed (3 times) with ethanol, then dried in a vacuum oven (DJF-6050, Guangzhou Kangheng Instrument Co., Ltd., PR China) at 50 °C for 6 h to get the cationic starch.

After that, 50% NaH_2PO_4/Na_2HPO_4 (total mass of the available phosphates is 10.00 g with the mass ration of $NaH_2PO_4{\cdot}2H_2O$: $Na_2HPO_4{\cdot}12H_2O$ = 0.87:1) was added to the flask containing the above cationic starch (5.00 g). The slurry was heated at 60 °C under agitation for 2 h, and then filtered. The filtered product was dried at 50 °C till the moisture content less than 15%, and put into microwave for 6 min similar to that described above. The mixture was thereafter cooled to room temperature and washed with ethanol until no color changed with the ammonium molybdate under heating. It was then dried in a vacuum oven at 50 °C for 6 h. Subsequently, it was pulverized and sieved, and the final amphoteric starch was obtained as a white powder. The synthetic pathway was shown in Scheme 1.

2.3. Synthesis of cationic starch with water bath heating

To confirm the microwave effects, cationic starch was synthetized with conventional water bath heating, and its synthetic processes were similar to those described in Section 2.2 except that the microwave treatment was substituted by the water bath with agitation at 80 °C for 2 h.

2.4. Characterization methods

2.4.1. Degree of substitution (DS) and phosphorus content

The degree of substitution (DS) was calculated from the nitrogen content according to the following equations in triplicate (Carr & Bagby, 1981):

$$\mathrm{DS} = \frac{162 \times N}{1400 - 151.5 \times N}$$

where N is the Kjeltech nitrogen content (%) and determined by the Kjeldahl method with a Kjeltech distilling unit according to the earlier literature (AOAC, 1990), 162 is the molar mass of anhydroglucose unit, 151.5 is the molar mass of hydroxypropyl trimethyl ammonium chloride group, and 1400 represents for 100 times of the nitrogen atomic mass.

The bond phosphorus content was assayed following Chinese National Standard (GB/T, 2008), and it was analyzed by a UV/Vis spectrophotometer (UV–VIS752, China) at 825 nm wavelength.

2.4.2. Swelling power and solubility index

The swelling power and solubility index were determined by the method described by Lin et al. (2011) with slight modifications. Starch (2.0 g dry base) was mixed in 60 mL distilled water at about 95 °C for 30 min. They were centrifuged at 3000 r/min for 15 min. Supernatant was decanted carefully and kept, and the wet starch residue was weighed for swelling power determination. Swelling power was the ratio of the weight of the wet sediment to the initial weight of dry starch. The solvent of the supernatant was evaporated at 105 °C for 5 h. The solubility index was determined from the ratio of the weight of the dried supernatant to initial weight of the dry starch. The experiment was repeated twice and the mean values were recorded.

2.4.3. Molecular mass and polydispersity

The weight-average molar mass (M_w) and polydispersity were determined using a gel permeation chromatography (GPC) system, consisting of a 515 HPLC pump (Waters Corporation, Milford, MA, USA) with a Dawn DSP laser photo meter (Wyatt Technology Corporation, USA), a Wyatt Optilab DSP interferometric refractometer (RI detector), an Agilent 1100 series variable wavelength UV detector, and a Sepharose TSK G3000SW gel column. The mobile phase was a 0.05 M phosphate buffer solution (pH 6.70) containing sodium azide (0.05%, w/v), and the flow rate was 0.8 mL/min. A starch sample dispersed in phosphate buffer solution was filtered through a 4.5 μm cellulose nitrate membrane prior to injection onto the

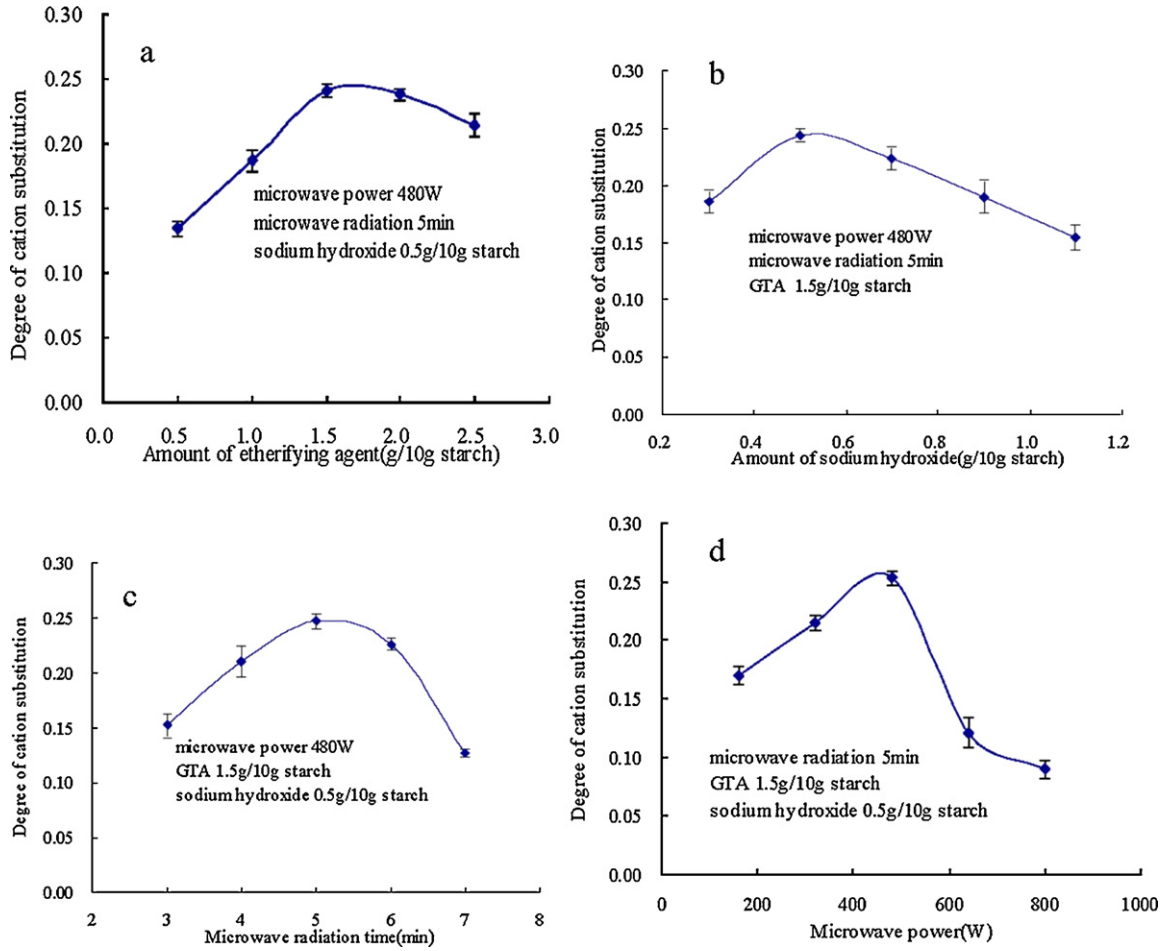

Fig. 1. (a) Effect of etherifying agent dosages on DSc, (b) effect of sodium hydroxide amount on DSc, (c) effect of microwave radiation time on DSc, and (d) effect of microwave power on DSc.

GPC column. The GPC/MALLS data were analyzed by GPC software (Astra 4.90.08 QELLS 2.XX, Wyatt). Duplicate tests were conducted for each sample.

2.4.4. FTIR analysis

A Thermo Nicolet FTIR Spectrophotometer (Model Nexus 870 FTIR) was used and the potassium bromide (KBr) pellet method used for FTIR study. The FTIR spectra of native starch, GTA, cationic starch and amphoteric starch were acquired after 32 scans between 4000 and 400 cm^{-1}, with spectral resolution of 4 cm^{-1}.

2.4.5. Scanning electron microscopy (SEM)

SEM images were observed on a HITACHI S-3400N scanning microscope. Each starch sample was suspended in a bottle in which there was a small amount of ethanol by ultrasonography. The sample was mounted on glass plates and dried for removal of the ethanol, followed by coating with a thin layer of gold in a vacuum before examination.

2.4.6. ^1H NMR spectroscopy

The starches were prepared for NMR experiments by following the method of Yue, Qinlu, Zhengxing, and Huaxi (2011) with modifications. The samples were prepared by adding double-deionized water of solid content and steam heating for 20 min in a closed-thermostat water bath, and then freeze-dried and ground to pass through a 100-mesh sieve. ^1H NMR spectra were acquired on a Bruker DMX 500 spectrometer (Bruker AVANCE III 500,Swiss) in DMSO-d_6 at 500.13 MHz for ^1H; all spectra were recorded at 25 °C (DMSO-d_6), with a concentration of about 1% (w/w).

2.5. Flocculation performance

2.5.1. Dosage on the flocculation effect

Typically, 50 mg of methyl violet was dissolved in 100 mL deionized water in a high-speed blender, and then water was added to the final volume of 1 L. 250 mL model water (50 mg/L methyl violet) was transferred into a 500 mL square beaker and the solution pH was adjusted to 11.0. Optimal amphoteric starch (DS 0.25, phosphorus content 4.35%, the same below) was added by mixing at 200 rpm for 3 min, 50 rpm for 5 min and quiescent settling for 30 min. After the settling period, a small sample was taken at half height of the liquid column for measurement of absorbance by a UV/Vis is spectrophotometer (UV–Vis752, China) at 552 nm wavelength.

2.5.2. pH value on the flocculation effect

The solution pH of the 250 mL model water was adjusted to 3.0, 5.0, 7.0, 9.0, and 11.0, respectively. A specified volume of flocculant determined from the previous test was added. Other procedures were similar to 2.5.1.

2.6. Adsorption performance

The adsorption capacities of amphoteric starch toward heavy metal ions were determined by the depletion method. The amount

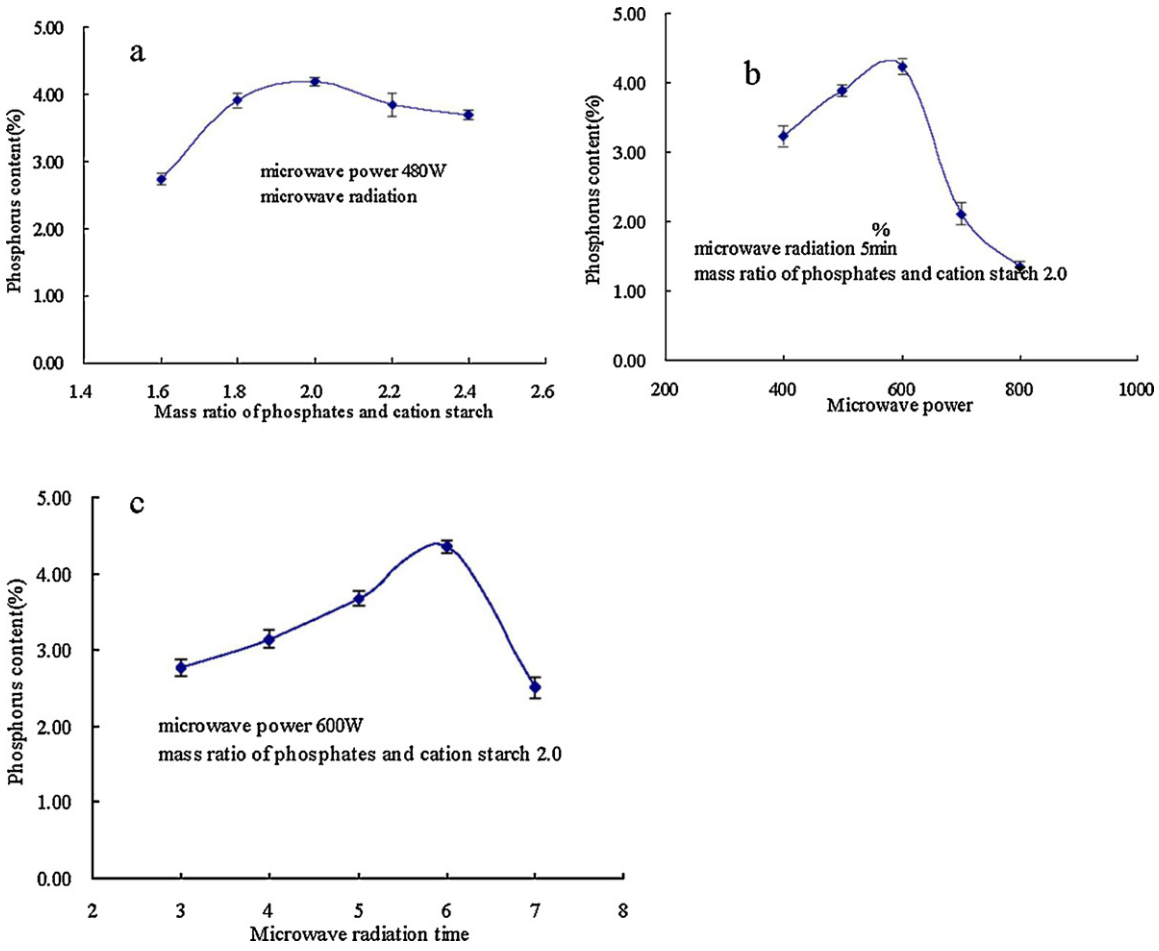

Fig. 2. (a) Effect of the mass ratio of phosphates to cation starch on phosphorus content, (b) effect of microwave power on phosphorus content, and (c) effect of microwave radiation time on phosphorus content.

of adsorbed Pb (II) ions (Q) was calculated using the difference between known initial Pb (II) ions concentration and concentration measured in supernatant.

$$Q = \frac{(C_0 - C_t) \times V}{m}$$

where C_0 and C_t are the initial and residual concentration of Pb (II) ions in the solution; V is the volume of the solution; m is the mass of the amphoteric starch, respectively.

2.6.1. Initial concentration on the adsorption effect

To study the effect of initial concentration of Pb (II) ions on the adsorption, the operating conditions were as follows: volume of solutions was 100 mL, initial pH of the solution was 5.0, dosage of amphoteric starch was 40 mg, concentration of Pb (II) ions was 10, 20, 30, 40, 50 mg/L respectively, which was prepared from native standard solution of 1 g/L (acidic), and the solution was gently shaken for 3 h at room temperature (25 °C). After 30 min of quiescent settling, a clarified layer of the liquid was formed. A small sample of the formed clarified liquid was removed for measurement of Pb (II) ions concentration using atomic absorption spectrophotometer (Hitachi Z-2000, Japan).

2.6.2. pH value on the adsorption effect

100 mL solution (50 mg/L of Pb (II) ions) was transferred into a 250 mL square beaker and the solution pH was adjusted to 5.0. 40 mg amphoteric starch was added. Other procedures were described above as that in Section 2.6.1.

All flocculation and adsorption experiments were carried out in duplicate. The data reported in the paper were the arithmetic average of the results derived from the repeats.

3. Results and discussion

3.1. Characterization of copolymer

3.1.1. Synthesis of amphoteric starch

Various grades of the copolymer were synthesized by varying the microwave power, microwave radiation time and reagent concentrations (GTA and phosphates). The mechanism of microwave assisted grafting is as follows:

The microwave radiation rotates the GTA molecules, leading to the severing of its epoxypropyl bond, and the pi bond electron cloud splits up into two localized clouds (i.e. free radical sites on the constituent carbon atoms) (Sumit et al., 2011). Moreover, the microwave is absorbed by the polar groups (e.g. —OH groups attached to starch molecule) which then behave as if they were anchored to an immobile raft and its immobile localized rotations will occur in the microwave region (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998), which eventually leads to the severing of these bonds, leading to formation of free radical sites. Through usual free radical reaction mechanism, the free radical sites created on the starch backbone and the GTA interact to yield the cationic graft copolymer. With the same mechanism, the free radical sites created on the cationic starch backbone and phosphates interact to yield the amphoteric starch under microwave radiation.

Table 1
Swelling power, solubility index of native starch and modified starches.

Samples	Swelling power ($g\,g^{-1}$)	Solubility index (%)
Native starch	22.63	10.5
Cationic starch	28.96	10.0
Amphoteric starch	31.55	8.1

The DS of cationic starch, synthesized from 1.5 g GTA per 10 g starch with microwave radiation (molar ratios of anhydroglucose unit (AGU) of starch:NaOH:GTA were 1:0.234:0.184), reached 0.26, and that from the same mixture with water bath heating was only 0.22. Obviously, even if the reaction time is prolonged to 2 h for conventional water bath heating method, lower DS is obtained. Thus, a shorter reaction time and higher thermal effect make microwave-assisted synthesis attractive for practical purposes.

3.1.2. Swelling power and solubility index

Both cationic starch and amphoteric starch had higher swelling power and lower solubility index than their native starch (Table 1). That is because cationization leads to structural reorganization owing to steric hindrance and repulsion between starch molecules, facilitating water percolation within the granule amorphous regions. Compared with cationic starch, amphoteric starch had higher swelling power and lower solubility, and this could be attributed to the presence of phosphate groups in the amphoteric starch that posses more water holding capacity (Lin et al., 2011).

3.1.3. Molecular mass and polydispersity

Compared to the native starch, the M_w and M_n values of cationic starch increased by 27.7% and 90.0%, moreover, for amphoteric starch those increased by 18.8% and 113.3% (Table 2). One explanation would be that intermolecular cross-links through free radical reaction, resulting in an increase in the molecular size, which is consistent with that reported by Chan, Bhat, and Karim (2009).

M_w/M_n is indicative of the extent of polydispersity. As the molecular weight distribution becomes broader, the value of M_w/M_n increases (Gowariker, Viswanathan, & Sreedhar, 1986). The increasing polydispersity of modified starch, compared to native starch, could be attributed to the formation of cross-linking as mentioned previously, and cross-linking index of different molecules change a lot. Thus the molecular weight distribution becomes broader and the polydispersity increases, which is more obvious for amphoteric starch (Table 3).

3.1.4. Value and phosphorus content

The DS of a starch derivative is defined as the number of hydroxyl (OH) groups substituted per D-glucopyranosyl structural unit of the starch polymer, with the possible maximum possible value of 3 (Fang, Fowler, Tomkinson, & Hill, 2002). It was showed the different factors affected the DS (Fig. 1). In the systems examined, similar clear trends were observed. Under the experimental conditions, the yield of DS increased with GTA amount, microwave radiation time and microwave power, approaching an asymptotic value to 0.24–0.26 and then decreased. The DS does not exceed the top value even with higher microwave power, because the microwave power higher than 480 W caused temperature to rise sharply, resulting in GTA decomposition and starch carbonization.

Table 2
Molecular mass determination of native starch and modified starches.

Samples	M_n ($\times 10^5$)	M_w ($\times 10^5$)	M_w/M_n
Native starch	1.12	3.01	2.69
Cationic starch	1.43	5.72	4.00
Amphoteric starch	1.33	6.42	4.83

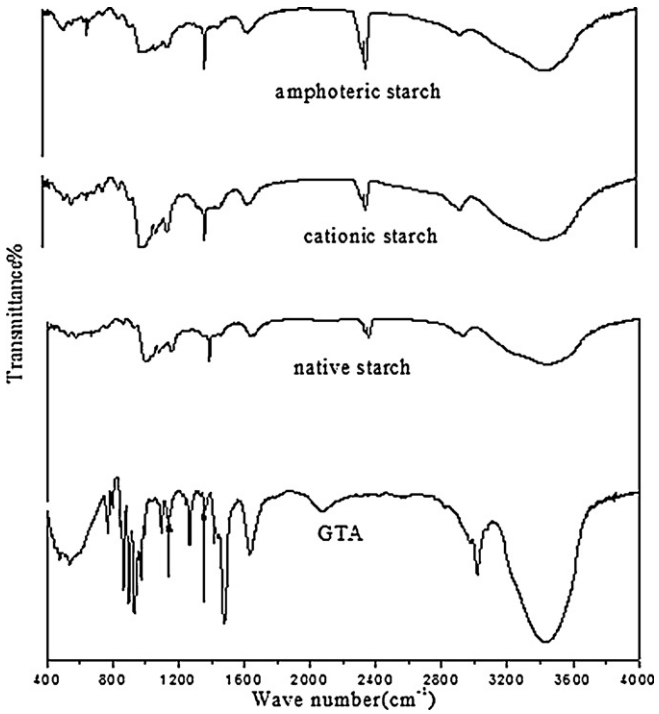

Fig. 3. FTIR spectra of GTA, native starch, cationic starch and amphoteric starch.

The starch esterification with nitrogen and phosphorus compounds is a very complicated process comprising a few concurrent reactions, like relatively deep, controlled degradation, slight substitution by phosphate and carbamate groups, neutralization, cross-linking (Lewandowicz et al., 2000). Here, the phosphorus content showed a similar trend with the nitrogen content detected for DS (Fig. 2). Under the experiment conditions, all these results showed the mutual reactions involved in the phosphorylated starch depended on microwave power and time, as well as the mass ratio of phosphates and cationic starch. When microwave power was 600 W, microwave radiation time was 6 min and the molar ratio of phosphate/AGU was 1.45, the phosphorus content reached the maximum (4.34%).

3.1.5. FTIR analysis

The FTIR spectrum of GTA, native starch, cationic starch and amphoteric starch was shown in Fig. 3. The characteristic peak ($-CH_2-\overset{+}{N}-(CH_3)_3$) for quaternary ammonium salt appeared at 862–923 cm^{-1} in cationic starch samples, and hydrocarbon absorption peak located at 2342 cm^{-1} and 2359 cm^{-1} while —C—O— absorption peak at 1161 cm^{-1} and 1384 cm^{-1}. In the case of amphoteric starch, besides the quaternary ammonium salt ($-CH_2-\overset{+}{N}-(CH_3)_3$) and ether linkage (—C—O—) located at 862–923 cm^{-1} and 1161 cm^{-1}, 1384 cm^{-1}, respectively, the presence of additional bands at 993 cm^{-1} and 1082 cm^{-1} assignable to the stretching mode of the stretching vibration peak (—P=O) and P—O—C, suggested that the amphoteric starch was an amphoteric compound which contains the cationic quaternary ammonium group as well as the phosphate ester group. All these data confirmed the formation of starch ethers and esters.

3.1.6. Scanning electron microscopy (SEM)

No coarseness or damage was observed on the surface of the native starch granules. The granule surface appeared smooth, oval, and irregularly shaped (Fig. 4a). In etherification reactions for cationic starch, granularity of the products was retained (Fig. 4b).

Table 3
FTIR values of GTA, native starch and modified starch.

Samples	—OH stretching (cm^{-1})	—CO stretching (cm^{-1})	—CH stretching (cm^{-1})	$—CH_2—O—CH_2$ stretching (cm^{-1})	—CN stretching	C—O—P stretching (cm^{-1})
GTA	–	1160,1384	–	–	866,930	–
Native starch	2931,3444	1159,1378	2344,2360	1082	–	–
Cationic starch	2930,3444	1161,1384	2342,2359	1080	862,923	–
Amphoteric starch	2930,3444	1162,1384	2342,2359	1080	861,930	993,1082

Small deformations seen on the surface of granules could indicate that etherification mainly occurred on the particle surface, which also agreed well with that modification of starch under microwave irradiation could not be occurred in amorphous region but in partial crystalline region (Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005). Additionally, the cross-link among the particles in amphoteric starch elongated the molecular chain (Fig. 4b and c).

3.1.7. ^1H NMR spectroscopy

Compared with the native starch, there existed an obviously absorption peak at 3.08 ppm for cationic starch and amphoteric starch (Fig. 5), which are attributed to hydrogen atoms from the N-methylene group. What is more, the absorption of hydrogen atom (3.367 ppm) had down-field shift at both cationic starch (4.080 ppm) and amphoteric starch (4.253 ppm) field, being along

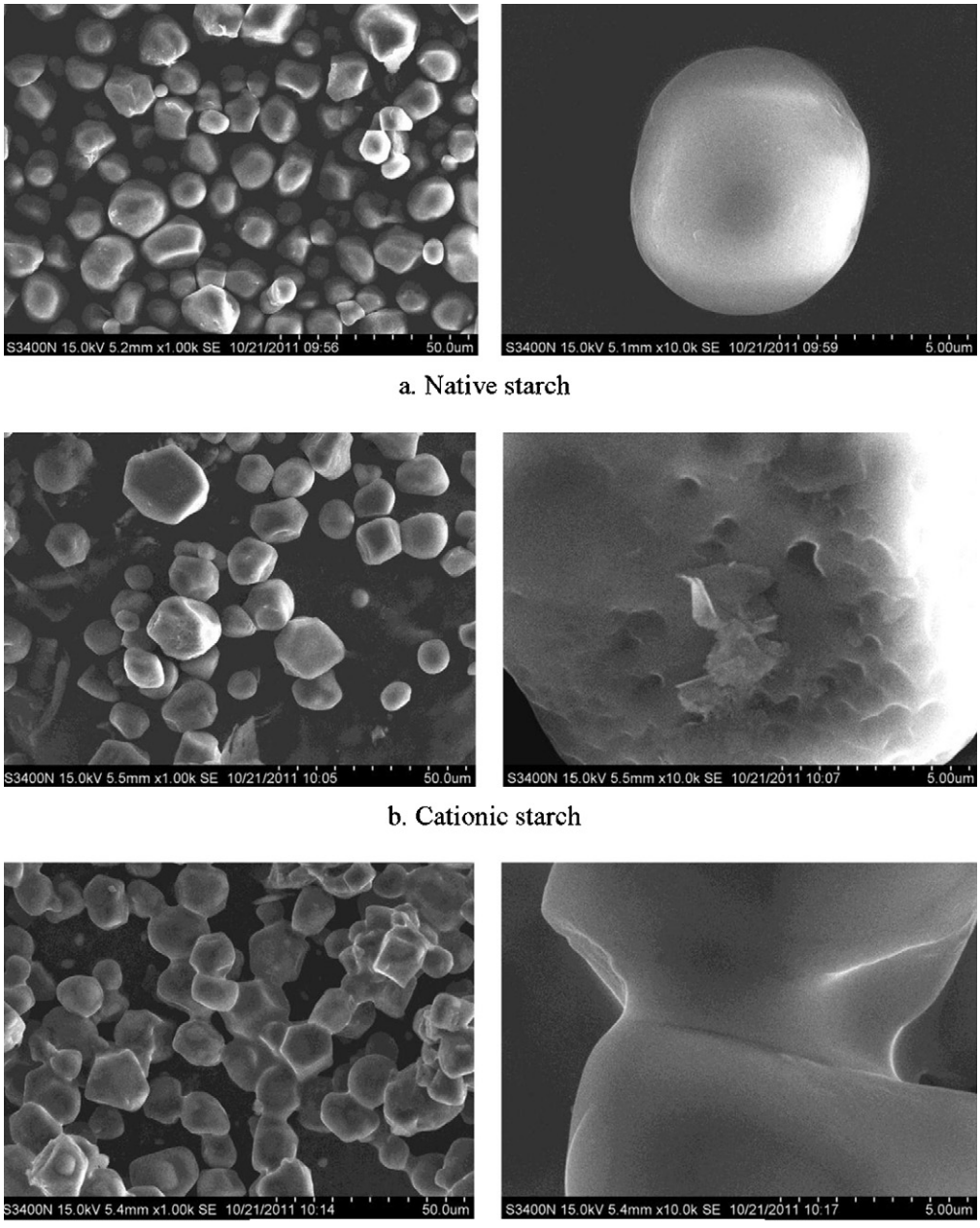

Fig. 4. SEM photos of native starch, cationic starch and amphoteric starch.

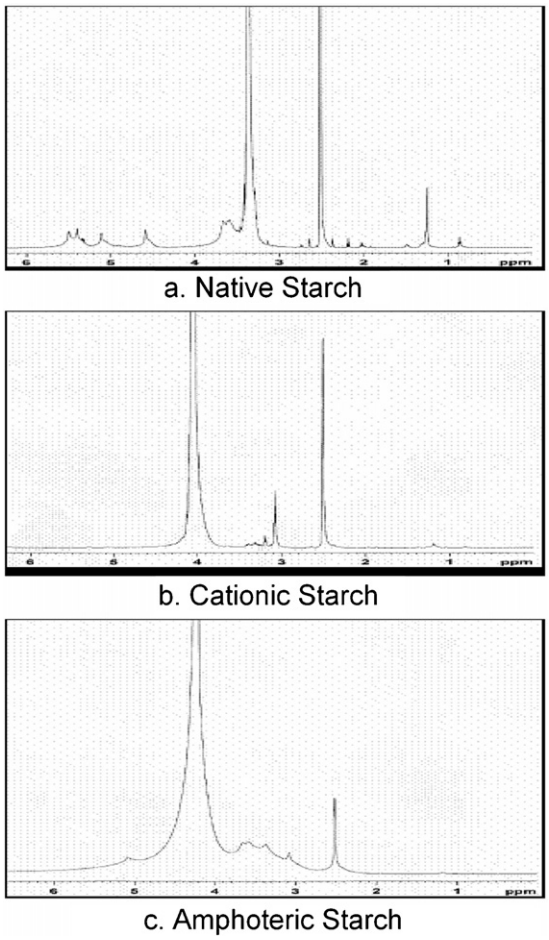

Fig. 5. ^{1}H NMR spectra of native starch, cationic starch and amphoteric starch.

with a much larger shift at amphoteric starch field. The main reason for these could be that the electron withdrawing inductive effect resulted from the strong electronegativity of the nitrogen atom, phosphorous atom and oxygen atom, which were grafted onto the native starch, promoted the low field shift of hydrogen atom. And it follows that etherifying agent and phosphate have been successfully grafted onto the polysaccharide backbone.

3.2. Flocculation performance

3.2.1. Dosage on the flocculation efficiency

The major mechanism of flocculation by polymers is bridging. The bridging takes place by adsorption of a polymer molecule at more than one site on a particle or at sites on different particles. For effective bridging to occur, the length of polymer chains should be long so that they can extend from one particle surface to another. The copolymer molecules with longer chains (Fig. 4c) would be more effective than with short ones (Fig. 4a and b), which is in conformity to other studies (Pal et al., 2005; Singh, Nayak, Biswal, Tripathy, & Banik, 2003). Fig. 6 shows that the degree of flocculation achieved could be markedly affected by dosing, and decolorization rate increased to the highest AS concentration of 300 mg/L, where the ion association between negative phosphate ester involved in AS and positive methyl violet molecules was relatively strong, and the flocculation mechanism was "electrostatic patch" (Mabire, Audebert, & Quivoron, 1984). Flocculation in this system could not exceed a certain optimum dosage of AS, and further additions resulted in lower efficiency. It was explained that there was no longer enough bare particle surface available for attachment of

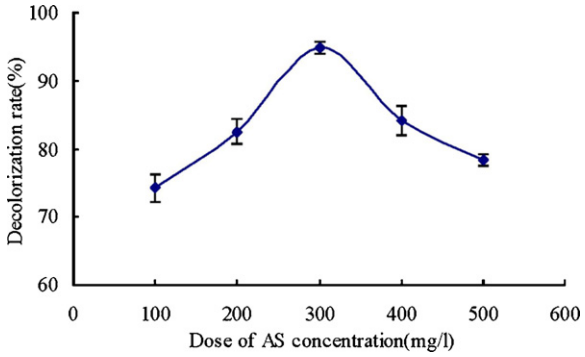

Fig. 6. Effect of AS dosages on the removal rate of color.

segments with excess polymer and the particles became destabilized, which might involve some steric repulsion (Tripathy & Ranjande, 2006). Thus overdosing might make the well-established suspension that was extremely difficult to separate, which was similar to the flocculation characteristics of kaolin suspension by polyacrylamide flocculants reported (Matsumoto, 2001).

3.2.2. pH value on the flocculation efficiency

The measured decolorization rate with 300 mg/L of AS dose at different pH conditions were presented in Fig. 7a. Decolorization rate was closely dependent on the pH value of the suspension, and it reached the minimum at pH 7.0, with 62.6% for decolorization rate. At this stage, AS reached its own isoelectric point, where inner salt bonds were formed between opposite electric charges involved in AS molecular chains. Therefore, the charge neutralization capacity to positive methyl violet molecules was attenuated significantly, resulting in low flocculation efficiency. In alkali conditions (pH > 7.0), the electronegativity of phosphate ester involved in AS was improved, which enhanced the charge neutralization capacities and the decolorization rate to positive methyl violet molecules.

3.3. Adsorption efficiency of copolymer

3.3.1. Adsorption time

The adsorption rate of copolymer was found to be very rapid during the initial 80 min and thereafter stayed at the plateau value (Fig. 7b). Since the adsorption process is a heterogeneous reaction, the complexation between Pb (II) and phosphate ester required a definite equilibrium time to get the maximum adsorption of flocculant.

3.3.2. pH value

Adsorption results in Fig. 7c indicated the amount of Pb (II) adsorbed increased with increasing pH. In strong acidic conditions (pH 2.0), the adsorption effect of Pb (II) was low. With the increase of pH, adsorption increased sharply until reaching a plateau. At relative low pH, the H^+ ions were much larger than Pb^{2+} ions on the surface of AS which limited the access of Pb^{2+} ions on the surface of the adsorbent. When pH increased, the effect of competition from H^+ ions decreased and the positively charged ions took their place on the surface. Phosphate esters in the AS appeared as target sites for the fixation of Pb (II).

3.3.3. Initial Pb (II) concentration

As shown in Fig. 7d, the adsorption capacities increased with increasing initial lead concentration. Considering the actual waste water, lower concentration of metal ions was employed in this work. In fact, the opportunity of collision between metal ions and phosphate esters increased with enhancing Pb (II) concentration

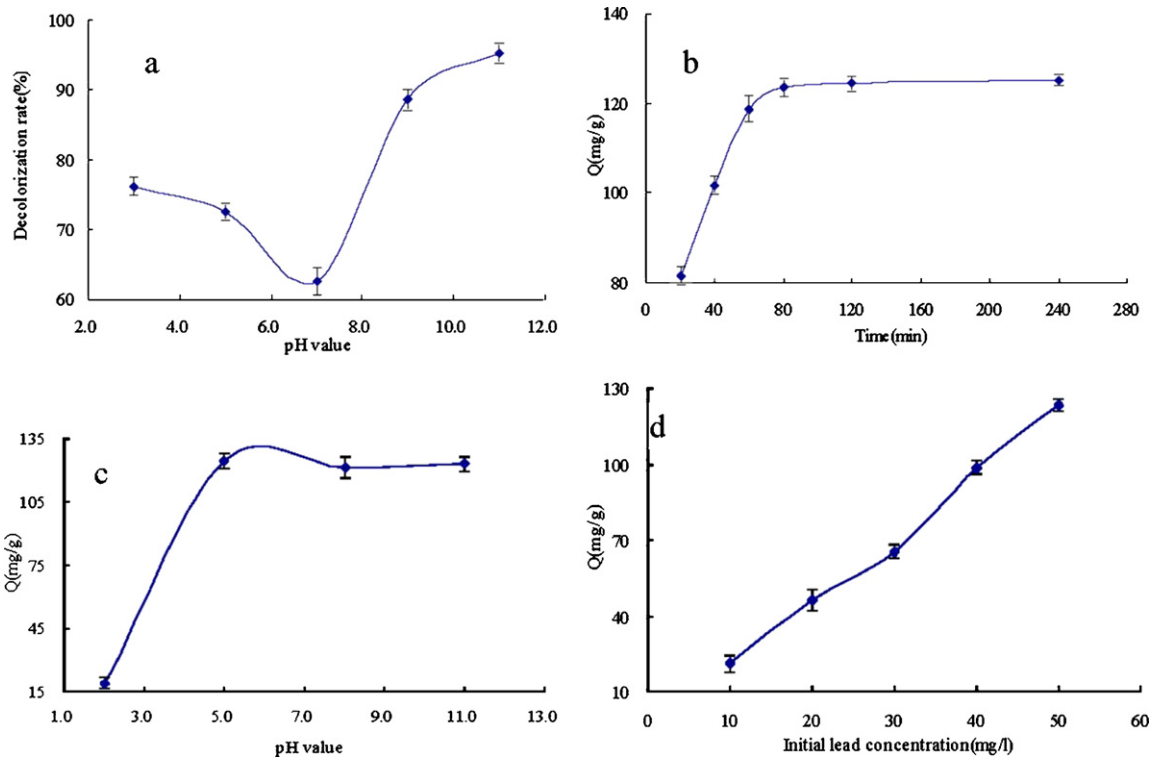

Fig. 7. (a) Effect of pH value on the removal rate of color with AS dosage at 300 mg/L, (b) effect of adsorption time on adsorption capacity with AS dosage at 400 mg/L and pH at 5.0, (c) effect of pH value on adsorption capacity with AS dosage at 400 mg/L and initial lead concentration at 50 mg/L, and (d) effect of initial concentration on adsorption capacity with AS dosage at 0.4 g/L and pH at 5.0.

under the same condition, which consequentially led to the higher adsorption capacity of the adsorbent.

4. Conclusion

A novel amphoteric copolymer flocculant was synthesized in two copolymerization processes under microwave radiation. The copolymer was characterized for the flocculation performance in terms of dosage and pH value, and absorption performance in the Pb (II). From the above experimental studies, it can be concluded that by incorporating a cationic moiety and an anion moiety on the backbone of starch, a modified naturally occurring polysaccharide, an effective flocculating agent can be developed for the treatment of wastewater.

Acknowledgements

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