Korean J. Chem. Eng., 35(7), 1500-1508 (2018)
DOI: 10.1007/s11814-018-0055-3

pISSN: 0256-1115
eISSN: 1975-7220

Flocculation of gelatinized starch: Flocculation performance and floc characterization

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(*Received 29 January 2018 • accepted 27 March 2018*)

Abstract−The removal of single macromolecules impurity is the basis study for the promotion of flocculation technology application in the Chinese herbal medicine solution purification. We applied the flocculation process to remove gelatinized starch in solution. Three types of cationic polyacrylamide (CPAM) with different charge density were used for flocculation of gelatinized starch solution. The flocculation performance was evaluated in terms of the amylose removal ratio (AMRR), the amylopectin removal ratio (APRR), total starch removal ratio (TSRR) and supernatant turbidity (ST). The flocs were characterized by sedimentation performance, Fourier transform infrared (FTIR), scanning electron microscope (SEM) and X-ray photoelectric spectroscopy (XPS) method. The experimental results show that the flocculant CN15 has the best performance for gelatinized starch flocculation among three flocculants. According to the characterization analysis, the flocs exhibited an obvious network structure, and it is concluded that hydrogen bonding between N-H in CPAM and C-O in the starch and bridging flocculation played the essential roles in flocculation of the gelatinized starch.

Keywords: Gelatinized Starch, Cationic Polyacrylamide, Flocculation, Floc Characterization

INTRODUCTION

Chinese herbal medicine solution is an important type of traditional Chinese medicine, which is obtained by decocting and concocting medicinal plants (root, stem, leaf, and fruit) for a certain time. Although this preparation method may extract the majority of the active components from the medicinal plants, it also brings out a large amount of other macromolecules which are not bioactive, such as starch, pectin, tannin and protein. These macromolecules not only have no effect, but also affect the clinical effect and stability of the Chinese herbal liquid, even leading to reducing the shelf life. Thus, it is highly demanded to purify Chinese herbal medicine solution. In fact, the first step of purification often lies in the removal of these macromolecules impurities in herbal liquid.

Ethanol precipitation is still the primary approach for practical herbal liquid purification with the purpose of removal of inactive macromolecule [1]. However, it has some disadvantages which affect the medicine yield and the clinical curative, such as long production period, high energy consumption, complex operation and high loss of active ingredients [2-5]. As one of the alternative purification methods for Chinese herbal medicine solution, flocculation technology draws intensive attention [6-8] because of its simpler procedure, lower cost and higher efficiency. Flocculation, as a primary purification technique to remove organic and inorganic finely dispersed solids particles from colloidal solution and suspension, has been applied successfully in many fields [9-13]. After flocculation, large and strong aggregates can be easily separated by conventional physical methods, such as filtration or settling. The application of flocculation technology has achieved some progress in purification of compound Chinese herbal medicine [6-8,14]; the effect of high tannin and protein removal ratio, high active component retention rate and low ST have been obtained. Since Chinese herbal medicine solution is an extremely complicated and mixed dispersion system, the flocculation mechanism of removing each macromolecular impurity is still not very clear. The study of the removal of single macromolecules is the basis for the promotion of flocculation technology in the purification of Chinese herbal medicine solution. The single macromolecule such as tannic acid, protein and pectin simulation solution flocculation has been made by our previous research [14-16]. As the most common type of carbohydrate in plants, starch becomes gelatinized during decoction process of herbals. Together with cooling of the herbals solution, the starch chains (amylose and amylopectin) in the gelatinized paste re-associate, which is collectively termed "retrogradation." Amylose and amylopectin content in different plants are different, and their durations of retrogradation are also different. Amylose can cause short-time retrogradation ,which lasts for several days, while amylopectin is attributed to long-term retrogradation, which is a much slower process lasting for several weeks or even longer period [17,18]. Retrogradation of gelatinized starch usually results in low quality of Chinese herbal medicine solution, and profoundly affects the turbidity and stability of the solution, and even leads to herbal liquid spoilage and shelf-life shortening. On the other hand, starch is not a medicinally active ingredient though it usually is used as the main component of food. Gelatinized starch is usually used as a flocculant [19-22] or grafted flocculant [23-27], but little related literature of gelatinized starch removal by flocculation has been reported. As for the selection of flocculant, the starch removal effect by CPAM was obvi-

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ous in our initial experiment. Although CPAMs are not suitable in herbal solution flocculation because of their toxicity to organisms, a basic study focusing on the interaction between starch and CPMA is feasible and necessary.

In this study, three types of cationic polyacrylamide (CPAM) with different charge densities were chosen as the flocculants for purification of single gelatinized starch solution and exploration of the interaction between flocculant and starch. The flocculation properties of CPAMs on total starch, amylose (AM) and amylopectin (AP) were studied, respectively. Dual-wavelength colorimetric method was used for amylose and amylopectin removal ratios determination. The flocculation performance was evaluated by four evaluation indexes: amylose removal ratio (AMRR), amylopectin removal ratio (APRR), total starch removal ratio (TSRR) and supernatant turbidity (ST). In addition, the starch flocs were characterized through sedimentation velocity, Fourier transform infrared (FTIR), microscope, scanning electron microscope (SEM) and X-ray photoelectric spectroscopy (XPS) technique, in order to reveal and investigate flocculation mechanism.

MATERIALS AND METHODS

1. Materials

Analytical grade reagents were used in all cases. The samples of CPAM were obtained from Beijing Xitao Co. Ltd. (Beijing, China). The average relative molecular weight of CPAM was 1.0×10^7-1.2×10^7. The native corn starch with starch content above 98% was purchased from Jiangtian Chemical Technology Co. Ltd. (Tianjin, China). The amylose content of the samples was 29%. The sample was directly used in experiments without any further treatment. Amylopectin Hydrate (Amylose free), from Waxy Corn, was bought from TCI Development Co. Ltd. (Shanghai, China). High purity amylose was obtained by N-butyl alcohol precipitation and recrystallization, and the sample met the requirements of national standard GB/T 15683-2008. PVSK (Polyvinysulfuric acid potassium salt, CAS 26837-42-3) was purchased from Aladdin (Shanghai, China) and used as the cationic reactants. The o-TB (Toluidine Blue O salt, CAS 92-31-9) was obtained from J&K (Shanghai, China). Hexadecylpyridinium chloride monohydrate (CAS 6004-24-6) was also obtained from Aladdin (Shanghai, China).

2. Main Apparatus

The main apparatuses in experiments were the six-spindle flocculation mixer (MY3000-6K, Qianjiang Meiyu Co. Ltd., China), UV/VIS spectrophotometer (UV-VIS 7500, Shanghai Tianmei Co. Ltd., China), micro electrophoretic instrument (JS94H, Shanghai Zhongchen Co. Ltd., China), turbidity meter (WGZ-100, Shanghai Optical Instrument Co. Ltd., China), and pH meter (PHS-3C, Shanghai Leici Co. Ltd., China).

3. Preparation of the Flocculant Solution

Three types of CPAM powder with a certain mass were dissolved in deionized water to prepare 0.05% (w/v) stock solution. The prepared flocculant solution was sealed and aged about 24 h at room temperature before each experiment.

4. Preparation of the Gelatinized Starch Solution

Corn starch powder was dispersed in deionized water, and the mixed solution was heated at 100 °C under stirring for 1.5 h to prepare 0.5% (w/v) gelatinized starch. The pH value and the zeta potential of starch solution at room temperature were 7.1 and −2.7 mv, respectively. The starch solution was freshly prepared for using in experiments.

5. Flocculation Experiments

The flocculation experiments were carried out in the six-spindle flocculation mixer. Each test with 250 mL of gelatinized starch solution was conducted in a 400 mL beaker. The mixtures were stirred rapidly at 250 rpm for 3 min, followed by slow stirring at 100 rpm for 1 min. Different dosages of CPAM were added into the starch solution at the beginning of rapid stirring. After slow stirring, the beakers were removed from the flocculation mixer and the starch flocs were allowed to settle for 1 h before analysis.

6. Sedimentation Performance Test

The flocculated starch suspension was transferred to a 250 mL measuring cylinder (height: 200 mm) for static sedimentation about 30 min. The settling curve of the upper interface between a clear supernatant and the suspension was drawn, for which slope ratio at every point was the settling rate at a corresponding time value.

7. Measurement of Starch Content

The total starch content was measured according to the dual-wavelength colorimetric method [28,29]. The content of AM and AP of the corn starch was determined as the protocols described in ISO 6647-1:2007 and JHM Hovenkamp-Hermelink [30]. Iodine-AP and iodine-AM complex with certain content were scanned by UV-VIS Spectrophotometer in the wavelength range of 400 nm-900 nm, as shown as Fig. 1. The measure wavelength (λ_1=630 nm) and reference wavelength (λ_2=433 nm) of AM, and the measure wavelength (λ_3=534 nm) and reference wavelength (λ_4=768 nm) of AP were determined by the mapping method. The linear relationship between the absorbance and the iodine-starch complex ($content_{iodine\text{-}AM}=4.4371\Delta A_{AM}+0.0908$, r=0.998) was achieved in the range of 2-70 mg/L for AM, and the standard curve equation ($content_{iodine\text{-}AP}=29.722\Delta A_{AP}+0.1593$, r=0.999) was got in the range of 5-100 mg/L for AP, respectively. The samples dyed with iodine were scanned at the selected wavelengths, and then the AM and AP content in the sample could be calculated by their standard curves, respectively. The total starch content was the sum of AM

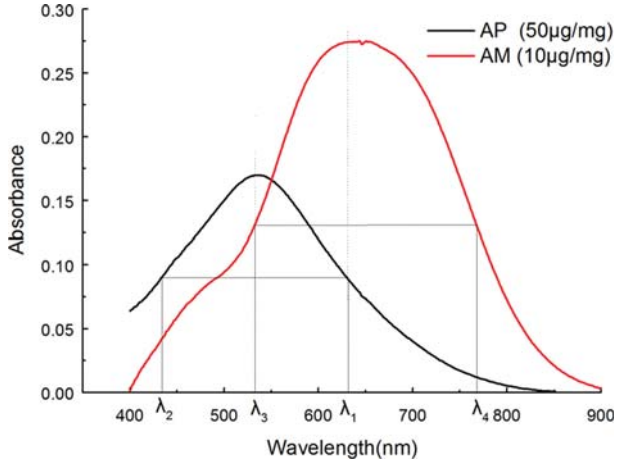

Fig. 1. Mapping constructions of the detection wavelength for AM and AP.

content and AP content.

The removal ratio of amylose amylopectin and total starch was calculated based on Eq. (1), respectively:

$$\text{removal ratio (\%)}=(C_{i0}-C_{it})/C_{i0}\times 100\% \quad (1)$$

where, C_{i0} denoted the initial concentration and C_{it} the impurity content ration at the end of a predetermined settling time (1 h) after flocculation operation.

8. Titration of Charge Density of the CPAM Solution

Colloid titration is based on the stoichiometric reaction between a polyelectrolyte with opposite electric charge, and the end point of the titration can be determined from the metachromatic color change of the indicator.

Polyvinylsulfuric acid potassium salt (PVSK) and Toluidine blue (o-TB) were dissolved in deionized water to prepare a 2.5×10^{-3} mol/L and 0.01% (w/v) solution, respectively. The PVSK solution was standardized by cetylpyridinium chloride. The titration endpoint was determined according to the solution color change from blue to red-violet, and the red-violet color of the solution remains about 1 min. The CPAM solution was titrated directly with PVSK. Together with 0.2 ml of the 0.01% o-TB solution, 1ml of the 0.05% CPAM solution and 9 ml of deionized water were added into a beaker. Then the PVSK solution was titrated into the beaker using a burette at about 1 mL/min. The whole titration procedure was performed under the magnetic stirring condition at 40 rpm.

The charge density (CD) of the CPAM solution was calculated as Eq. (2):

$$CD=\frac{(V-V_0)\times C}{m} \quad (2)$$

where CD is the charge density (mmol/g), C is the concentration of PVSK (mol/L), V is the volume of PVSK instilled in the solution of CPAM at the titration endpoint (mL), V_0 is the volume of PVSK instilled in the blank solution at the titration endpoint (mL), and m is the solution mass of CPAM (g).

9. FTIR Spectrum Measurement

FTIR spectrum was measured to investigate the flocculation mechanism. The settled flocs obtained from the flocculation experiment were collected and freeze-dried for FTIR analysis. The FTIR samples were prepared by mixing the freeze-dried flocs with an aliquot amount of spectroscopic grade KBr, and pressing to thin pellets. FTIR spectra of the samples were recorded by the Nexus 670FTIR spectrometer (Thermo Nicolet Corporation, USA).

10. Morphology Characterization

Morphology studies can provide information on micro-structure of flocs, so the surface morphology of starch and flocs was evaluated by microscope and SEM. The microimages of the wet flocs were recorded with the Olympus BX40 optical microscope matched a digital camera. The SEM images of the freeze-dried flocs in the experiments were photographed with the Merlin compact scanning electron microscope (ZEISS, German).

11. X-ray Photoelectron Spectroscopy (XPS) Measurement

To further verify the interaction between starch and flocculant, X-ray photoelectron spectroscopy (XPS) measurement of starch and flocs was performed in PHI Quantera II system (Ulvac-Phi, Japan) with Al Kα (hν=1,486.6 eV) X-ray source. The energy of the entire spectrum spanned from 1,100 to 0 eV with a scanning step of 1 eV. The high-resolution spectrum of the C1s in the region between 280 and 293 eV was collected at intervals of 0.025 eV.

RESULTS AND DISCUSSION

1. Effect of the Flocculant Dosage and its Charge Density

The flocculant dosage is a significant factor affecting the floccu-

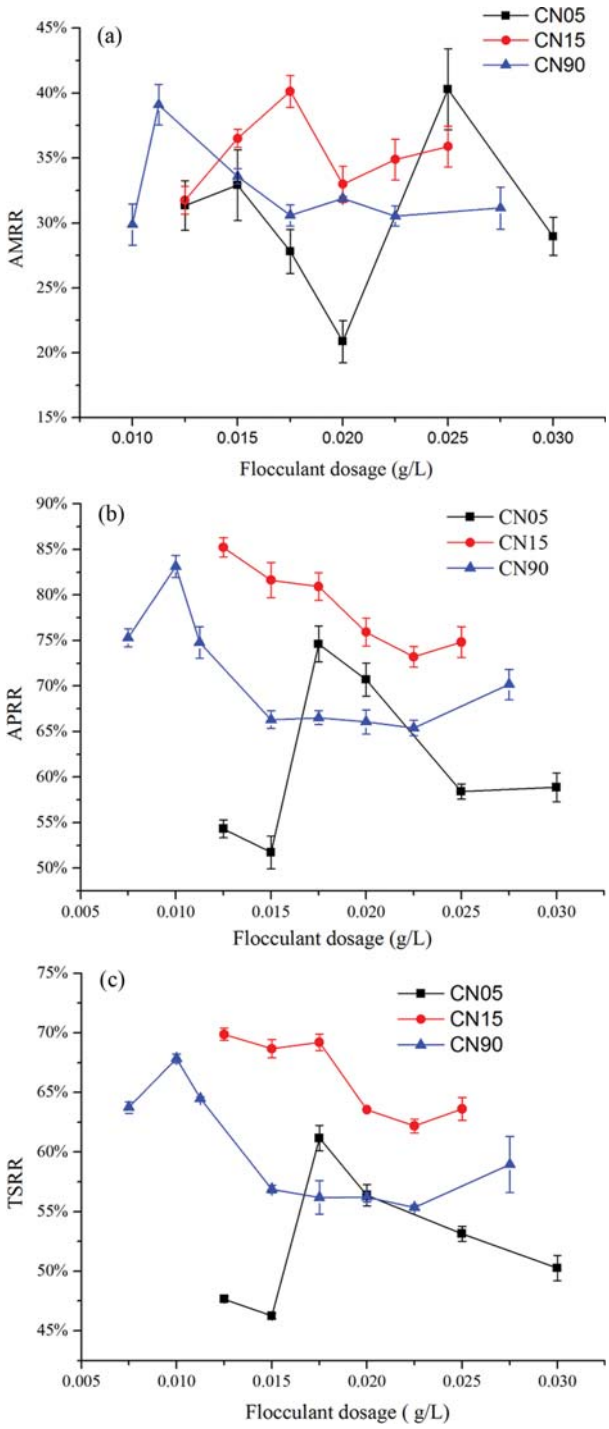

Fig. 2. Effect of the flocculant dosage on AMRR (a), APRR (b) & TSRR (c).

lation performance, which is dependent on the ST and the starch removal ratio. In this section, different cationic polymers CN05, CN15 and CN90 with charge densities of 1.87 mmol/g, 3.63 mmol/g and 9.68 mmol/g, respectively, were used in flocculation of gelatinized starch.

Fig. 2 and Fig. 3 show that AMRR, APRR, TSRR and ST fluctuated with rise dosage of three flocculants. It is generally known that the dissociation constant of the gelatinized starch in solution is 12.6 at 25 °C [31], and the hydrolyzed starch is slightly anionic [32] due to many -OH groups on its molecular chains [33,34]. Since the long chain of CPAM with superhigh molecular weight could offer a large number of available adsorption sites, the gelatinized starch molecules were adsorbed onto active sites of the adding flocculants by electrical neutralization. With the increase of CPAM dosage, the charge neutralization and the bridging ability were promoted. Optimal results of AMRR, APRR, STRR and ST should be obtained under appropriate dosage of CPAM. However, excessive flocculant dosage would cause mutual repulsion among the starch particles, which easily results in the generation of small size starch flocs and further a bad flocculation performance. It is clear that APRR was higher than AMRR in Fig. 2(a) and Fig. 2(b); the reason is not only the higher content of AP in starch but also the branch chain structure of AP which was more easily captured by the flocculant than the lined chain of AM. As shown in Fig. 2(b) and Fig. 2(c), the STRR variation trend was similar to that of APRR owing to higher AP content in total starch. The flocculant CN15 showed the best flocculation performance among three flocculants. When optimum CN15 dosage of 0.0175 g/L was used, the supernatant turbidity of the flocculated starch solution was 17.8 nephelometric turbidity units (NTU); meanwhile, the removal ratio of amylose, amylopectin and total starch was 40.1%, 80.9% and 69.2%, respectively.

In fact, the charge densities of CN05, CN15 and CN90 increased in turn. However, the flocculant CN15 showed best flocculation performance in contrast to CN05 and CN90, which indicated that adequate charge density could promote charge neutralization effect, but excessive charge density of CN90 could deteriorate flocculation performance due to the formed smaller flocs. Larger flocs were difficult to form by means of repulsive force, so a high supernatant turbidity was shown in Fig. 3. Therefore proper charge density of the flocculant was very beneficial for achievement of a satisfied flocculation performance.

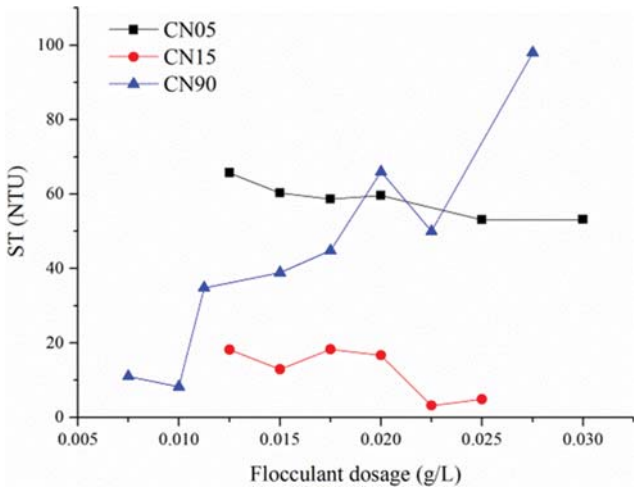

Fig. 3. Effect of flocculants dosage on the supernatant turbidity.

2. Settling Characteristics of the Flocculated Starch Flocs

As shown in Fig. 4, the settling velocities of the starch flocs flocculated by three flocculants were revealed through sedimentation curves. The sedimentation curve of flocculant CN15 was lower than that of other two flocculants. Adding flocculant CN15 at the best dosage could heighten the settling performance of the flocs. Natural sedimentation, i.e., retrogradation without anything added, is a slowly process; there was no clear interface formation between

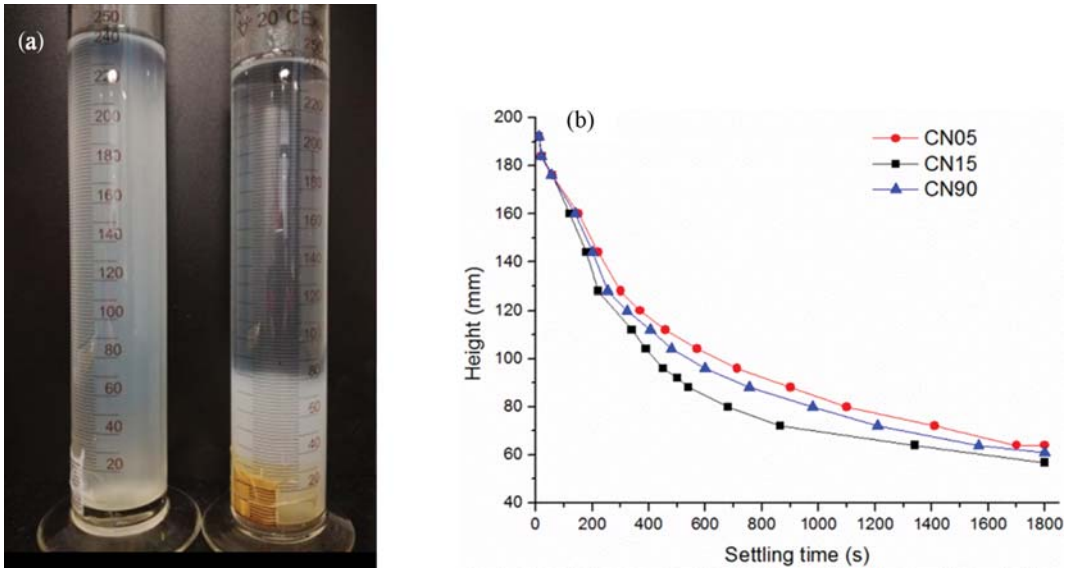

Fig. 4. Settling performance of the gelatinized starch: Natural sedimentation (left) and settling after flocculation with CN15 in 30 min (right) (a), the settling curves of the gelatinized starch flocculated with three flocculants (b).

supernatant and suspension in the range of 30 min. The added flocculant greatly accelerates sedimentation of the starch particles. This phenomenon could be illustrated by large flocs formation which made settling faster. When the flocculant was added, the gelatinized starch solution became unstable and small original flocs formed by flocculation adsorption. However, most of the original flocs were too small to settle naturally depending on gravity. Further collision, bridging and aggregation made the flocs grow bigger enough to settle through gravity. At this time because of the different floc size and density caused by different flocculants, the settling velocities were not the same, obviously. The interface between supernatant and suspension formed rapidly. When it sank, the big flocs could "clear" the small ones. The faster the interface dropped, the quicker the flocculation process completed, and the better the flocculation performance obtained. Obviously, settling performance was affected by flocculant type and charge density in our test.

3. FTIR Analysis

To study the interaction between the flocculant and the gelatinized starch, the FTIR spectra of three flocculants and their flocs as well as native corn starch were shown in Fig. 5.

It was found in Fig. 5(a) that a broad peak at 3,433 cm^{-1} was due to the stretching of the N-H asymmetric and the N-H symmetric of the NH_2 group. Two bands at 1,654 cm^{-1} and 1,319 cm^{-1} were attributed to the C=O stretching vibration and the C-N stretching. The peak at 952 cm^{-1} was assigned to the quaternary ammonium group [23], which was the cationic group in the CPAM molecular chain. The intensity of the peak at 952 cm^{-1} reflected the charge density of CPAM. The highest charge density was CN90 and the lowest was CN05.

As seen in Fig. 5(b4), the corn starch had a broad O-H stretching peak centered at 3,321 cm^{-1} and C-H stretching peak at 2,930 cm^{-1}. The peaks at 1,640 cm^{-1} are due to the bound water in the amorphous regions of starch [35,36]. In Fig. 5(b), both the corn starch and its flocs flocculated by CPAMs presented characteristic bands at 929 cm^{-1} and 762 cm^{-1} which were attributed to the skeletal mode vibrations of α-1,4 glycosidic linkage (C-O-C) and vibrations of symmetrical ring, respectively. These results indicated that the corn starch was presented in the flocs, and also confirmed that the basic structure of the corn starch was not changed, which could reflect the flocculant's bridging role. In Fig. 5(b1)-(b3), the

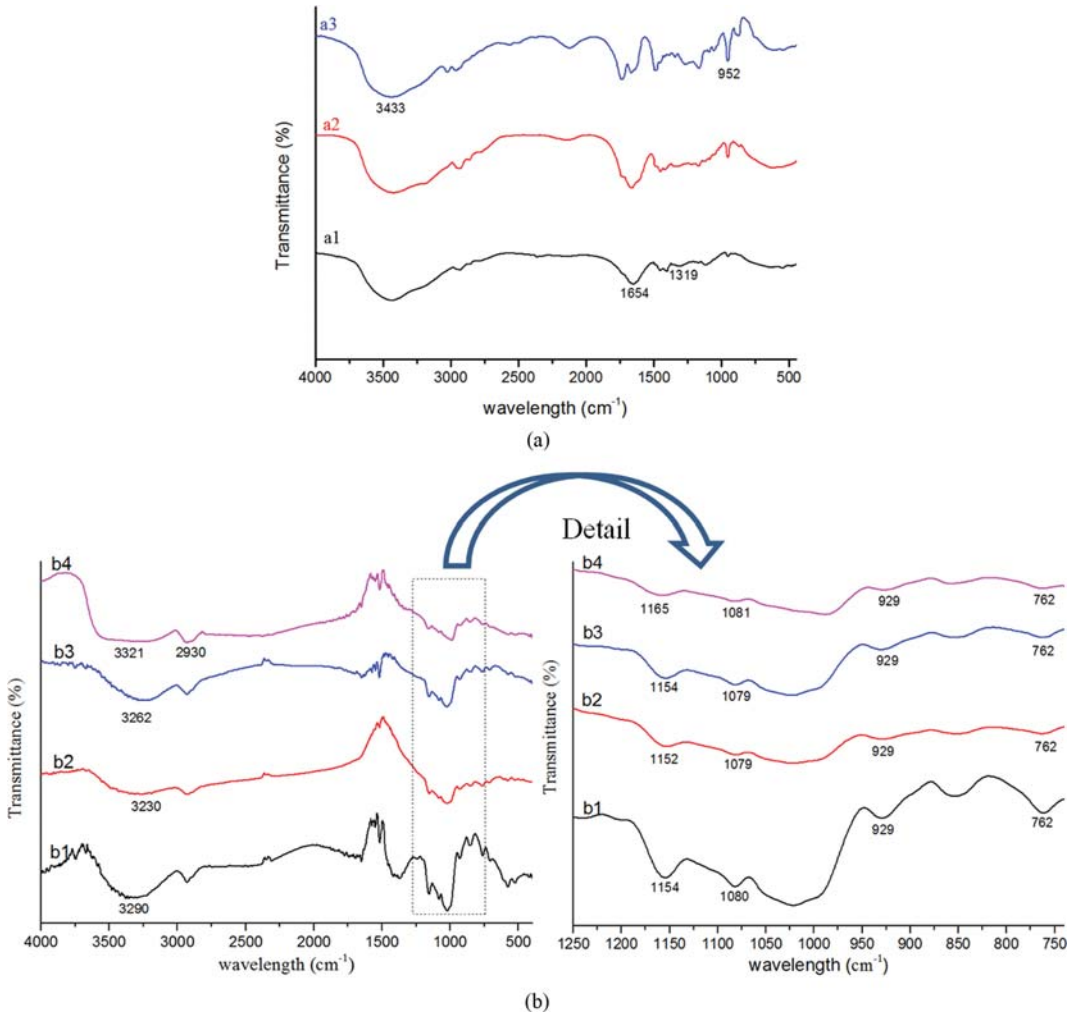

Fig. 5. The FTIR spectra of flocculants and starch flocs. (a) The FTIR spectra of the flocculants CN05 (a1), CN15 (a2) and CN90 (a3). (b) The FTIR spectra of the starch flocs flocculated by CN05 (b1), CN15 (b2), CN90 (b3) and native corn starch (b4).

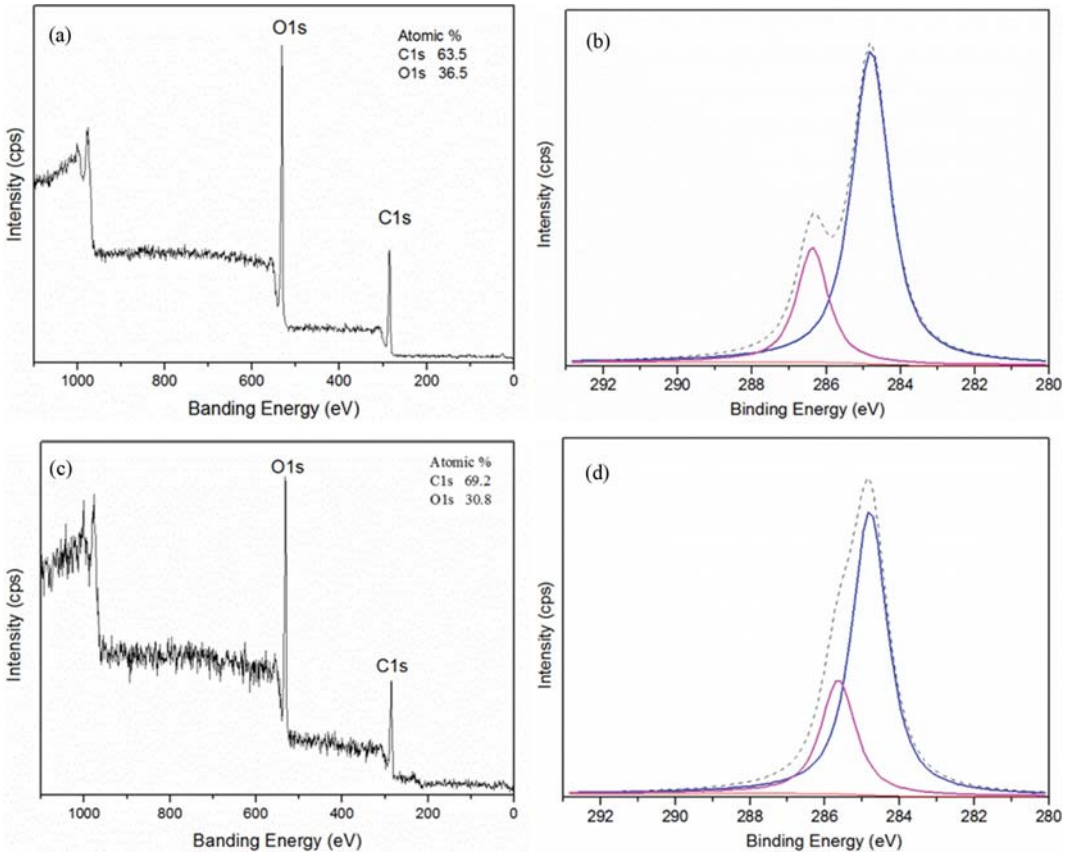

Fig. 6. The XPS patterns of the native corn starch (a), (b) and its flocs flocculated by CN15 (c), (d).

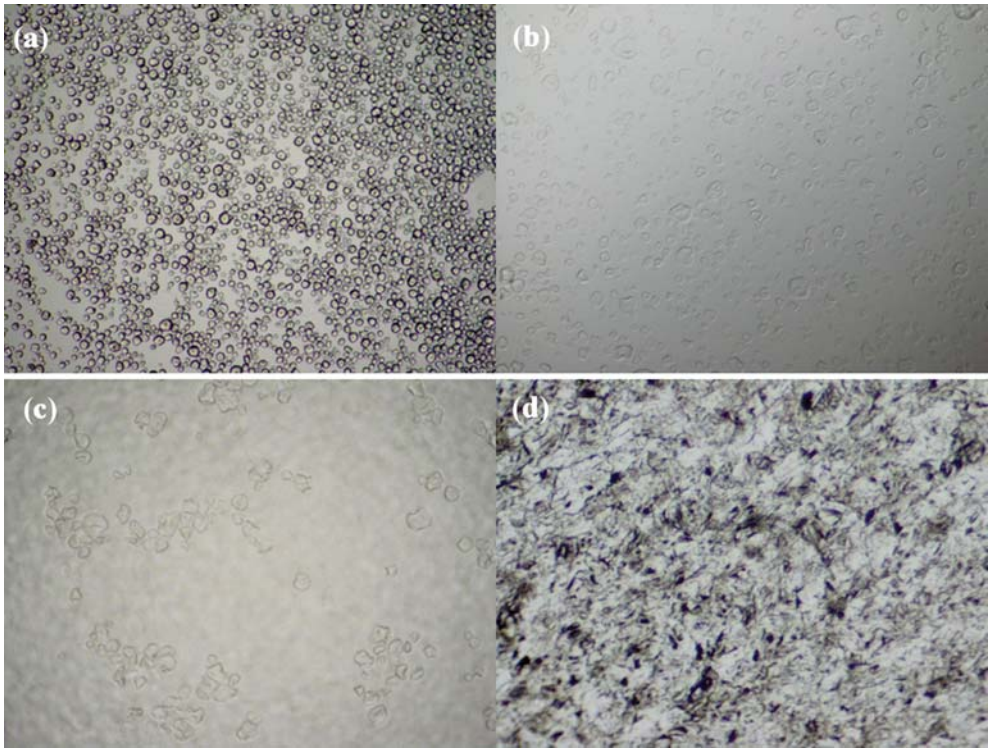

Fig. 7. Microscope photographs (×10) of the native corn starch in water (a), the gelatinized starch (b), retrogradation of the gelatinized starch (c), and the flocs of the gelatinized starch flocculated by the flocculant CN90 (d).

O-H stretching peaks at 3,321 cm^{-1} of the corn starch were shifted to 3,230-3,290 cm^{-1}, which could be due to strong hydrogen bonding formed between CPAM and the starch. The peaks at 1,158 cm^{-1} and 1,081 cm^{-1} for the starch was due to C-O and C-C stretching [37], which shifted to 1,152-1,154 cm^{-1} and 1,080-1,079 cm^{-1}, indicating that the bonds were elongated by the hydrogen bonding. These results pointed out that H-bonding would be one of the most important interactions between the starch and CPAM, as stated by other authors [37].

4. XPS Analysis

We used XPS to characterize the native corn starch and its flocs flocculated by CPAM. In Fig. 6(a), (c), the major elements of carbon and oxygen are presented in the XPS spectra of the native starch and its flocculated flocs, which appeared at about 285 eV and 532 eV, respectively. Nitrogen did not appear in the flocs spectrum, which could be due to its low content. The relative content of carbon and oxygen was 63.5% and 36.5% for the native starch, but 69.2% and 30.8% for the starch flocs. Increase of the carbon content and reduction of the oxygen content were due to a small amount of CPAM in the flocs and the high C/O ratio of CPAM. The C1s signal in the XPS spectrum was deconvoluted into two peaks, as shown in Fig. 6(b), (d). For the native corn starch, its XPS spectra showed two peaks corresponding to C-H/C-C at 284.8 eV and $C_{2\text{-}6}$-O at 286.4 eV [38,39]. Also, the binding energy at about 284.8 eV and 285.6 eV for C1s in the flocs spectrum and their corresponding chemical state was C-H/C-C and $C_{2\text{-}6}$-OH, respectively. The C-O peak in the starch flocs is 0.8 eV lower than the peak in the corn starch, which could be attributed to hydrogen bond between N-H in CPAM and C-O in the starch. This result confirmed that the H-bonding played an important role in the interaction of the flocculant and the starch.

5. Morphology Analysis

Morphology analysis provided information about micro-structure of the corn starch and its flocs. The native starch presented a granule shape in Fig. 7(a), and the gelatinized starch was obviously swelled bigger as shown in Fig. 7(b). After absorbing water, the

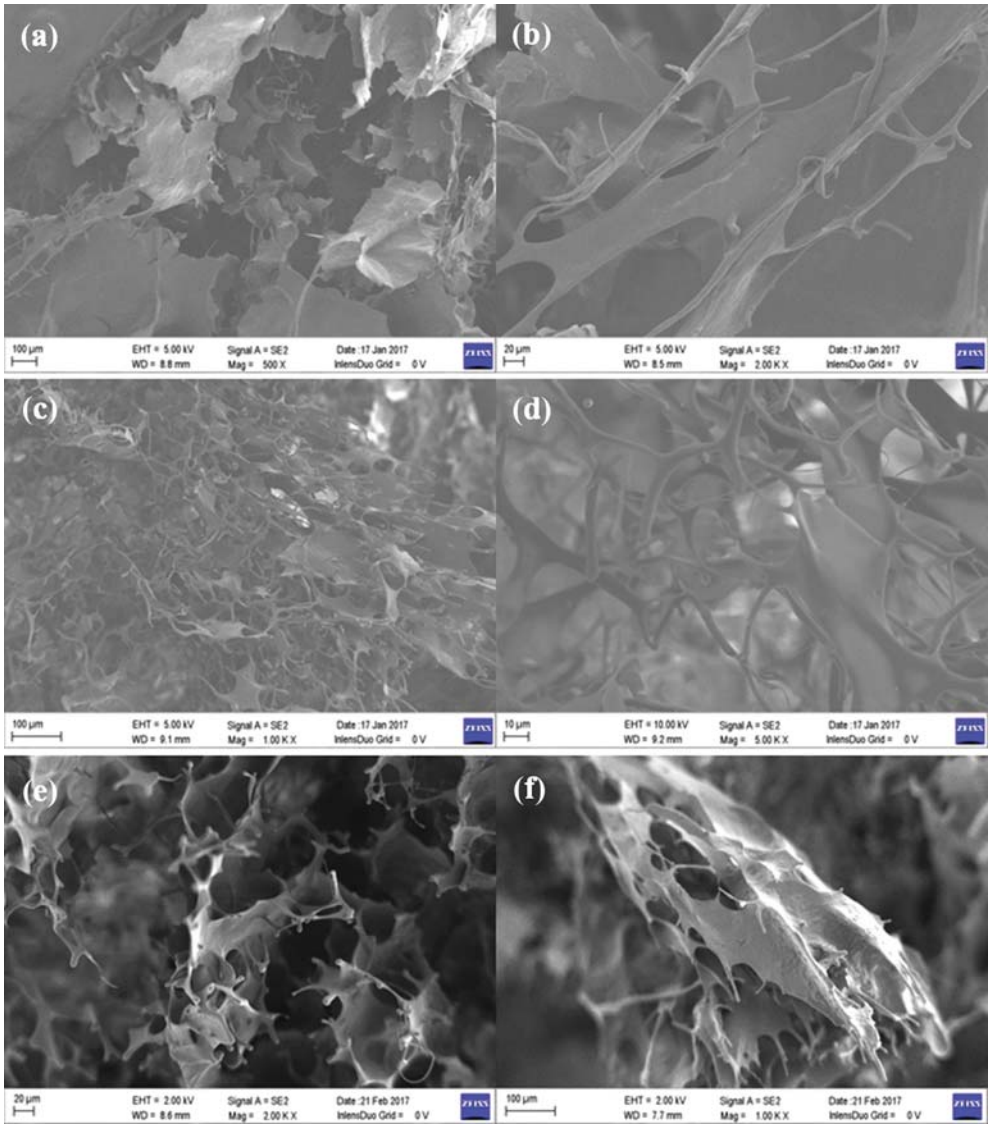

Fig. 8. SEMs of the starch flocs flocculated by the flocculant CN05 (a), (b), CN15 (c), (d) and CN90 (e), (f).

starch particles were swelled and ruptured. Retrogradation of the gelatinized starch was aggregated by the intermolecular forces. The state of the gelatinized particles aggregation is shown in Fig. 7(c), and the flocs morphology of the gelatinized starch flocculated by the flocculant CN90 is shown in Fig. 7(d).

In Fig. 8, SEM analysis revealed the morphology of the starch flocs. The flocs exhibited an obvious network structure, which indicated the full play of bridging effect. The flocs formed by the CN15 presented a "bird nest" structure with a complicated and intricate framework compared to that formed by CN05 and CN90, which revealed that the chain of the flocculant molecular was fully extended. The greater the flocculant extent, the higher the contact probability between starch and CPAM would be. The aggregated starch flocs grew bigger and intricate with the occurrence and gradual evolution of bridging flocculation. Complex network structure of flocs formed by CN15 brought out best flocculation performance.

CONCLUSIONS

Three types of CPAM were used for flocculation of gelatinized starch in water. The flocculation performance and the flocs characterization were studied. The flocculant CN15 with 3.63 mmol/g charge density showed best performance for both high total starch removal ratio and low supernatant turbidity. When the dosage of CN15 was 0.0175 g/L, the supernatant turbidity of the flocculated starch suspension was 17.8 NTU, and the removal ratio of the amylose, the amylopectin and total starch was 40.1%, 80.9% and 69.2%, respectively.

According to the flocculation performance and the flocs characterizations analysis, appropriate charge density of the flocculant is essential to achieve satisfactory flocculation performance (low turbidity and high removal ratio) and excellent the settling performance. The flocs exhibited a clear three-dimensional network structure, which revealed that the flocculant played a full role in generating a bridge during the flocculation process. Hydrogen bonding interaction between N-H in CPAM and C-O in the starch as well as bridging behavior played the essential roles in flocculation of the gelatinized starch.

By the study of single macromolecular impurity removal by flocculation and mechanism reveal between starch and flocculants, synthetic super-biopolymer with high effectiveness in removing various types of macromolecules simultaneously would become true, which will push forward the flocculation method applied to Chinese herbal medicine solution.

ACKNOWLEDGEMENTS

This work was financially supported by the National Nature Science Foundation of China (21276195) and the National Important Special Project of Pharmaceutical Innovation of China in the Eleventh Five-year Plan Period (2009ZX09301-008).

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