



Preparation and flocculation properties of cationic starch/chitosan crosslinking-copolymer

Lijun You, Feifei Lu, Dan Li, Zhongming Qiao, Yeping Yin*

Department of chemistry, College of Science, Huazhong Agricultural University, Wuhan, 430070, China

ARTICLE INFO

Article history:

Received 30 April 2009

Received in revised form 23 June 2009

Accepted 23 June 2009

Available online 30 June 2009

Keywords:

Crosslinking-copolymer

Flocculant

Transmittance

COD

SS

ABSTRACT

A novel flocculant (CATCS) based on corn starch and chitosan was prepared and its flocculation behaviors were studied. The synthesis conditions of CATCS were discussed and the production obtained was characterized using Fourier infrared spectra and scanning electron microscopy. Flocculation properties of the products were evaluated in terms of transmittance, removal of organic contaminant and solid suspending substances. Influences of temperature, pH and flocculant dosage on flocculation efficiency of CATCS were examined. CATCS had better flocculation performance at lower temperature for the wastewater investigated. CATCS showed better flocculation performance than cationic starch and chitosan in 5 g/L kaolin suspension trended to performance well in acidic and alkaline solution. The comparison of the flocculation performance between CATCS, $\text{Fe}_2(\text{SO}_4)_3$ and polyacrylamide showed CATCS had much efficient flocculation performance. In addition, cationic starch was prepared from corn starch using microwave-assisted method.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Flocculants are the materials, which are used, in fast solid–liquid separations by an aggregation process of colloidal particles; the process is termed as flocculation [1]. It is extensively used in the fields of fermentation processes, papermaking processes, food manufacturing and water treatment, etc. The flocculants used in water treatment can be classified into three groups: inorganic flocculants such as alum, ferrite flocculants or polyaluminum chloride; synthetic organic flocculants such as polyacrylamide derivatives; occurring flocculants such as sodium alginate or microbial flocculants [2]. Among these flocculants, the use of alum usually leads to the problem of residual aluminum [3,4]. Ferrite flocculants can be costly and the resultant excess iron may cause unpleasant metallic taste, odor, color, corrosion, foaming, or staining [2]. Although the synthetic organic flocculants are most frequently used because of their cost-effectiveness, they give rise to environmental problems in that they are not readily biodegradable and some of their degraded monomers such as acrylamides are neurotoxic and even show strong human carcinogenic potential [5]. In many countries, the disposal of flocculated sludge with polyacrylamide derivatives has been limited and will be strictly prohibited [6]. Because of the limitations of these flocculants, substitutes natural polymers such as starch, chitosan, cellulose, konjac glucomannan,

etc., are investigated as an attractive alternative because natural polymers and their derivatives are biodegradable as well as their degradation intermediates are harmless to human beings and environment.

As an important derivative of starch, which is one of the most abundant natural polymers in the world, cationic starch find wide applications in fields such as paper making, spinning, petroleum well drilling, medicine, daily chemicals and floatation [7–9]. Cationic starch derivatives possessing positively charged groups (such as amino, imino, ammonium, etc.) were effective flocculants over a wide range of pH [10]. They are non-toxic, easily biodegradable and can be used to treat organic and inorganic matter in wastewater carrying negative charge [11]. In addition, introduction of a cationic group to starch gives good mineral binding properties. Conventionally cationic starch is prepared in aqueous base or organic solvents. However, in the abovementioned process a large amount of solvent has to be used and serious environmental pollution may be caused. Also, the chain length of cationic moiety was limited [1]. Microwave-assisted synthesis has attracted considerable attention in recent years [8,9,12]. Compared with the conventional mode, a microwave-assisted reaction has advantages of energy saving, high conversion, and rapidity. The avoidance of volatile organic solvents in organic syntheses is the most important goal in green chemistry. During ultrafast synthesis using microwave irradiation, reactions are completed in minutes compared to hours and days using the conventional methods [13,14]. Thus, the cationic starch was synthesized with microwave-assisted method in this paper.

* Corresponding author. Tel.: +86 27 87284018.
E-mail address: ylyjyoy@yahoo.cn (Y. Yin).

Nomenclature

CATCS	the flocculant product we prepared
St	corn starch
Cat St	cationic starch made by corn starch
CS	chitosan
PAM	polyacrylamide
FT-IR	Fourier-transform infrared spectra
SEM	scanning electron microscopy
ω (Cat St)	mass of cationic starch (g)
ω (CS)	mass of chitosan (g)
COD	organic contaminant
SS	solid suspending substances
ω (Cat St): ω (CS)	mass ratio of cationic starch to chitosan

Chitosan is an N-deacetylated derivative of chitin, the second most abundant natural organic resource only next to cellulose on the earth [15]. It is widely distributed in arthropods, crustaceans, fungi, and yeast [16]. Because of the inter- and intra-molecular hydrogen bonding, chitosan can be dissolved in only acidic solution through the interaction between H^+ and $-NH_2$. This might accelerate its degradation and consequently reduce its flocculent efficiency [17]. In order to sort out this problem, a lot of work has been conducted on the modification of chitosan [18–20]. Among various modification techniques for chitosan, crosslinking is recognized as a most promising one because the abundant amino groups and hydroxyl groups in chitosan backbone could react with other activate function groups. Chitosan, however, as a flocculant for treating water, will have a higher cost than that of the traditional chemical flocculants [18]. Crosslinking cationic starch on to chitosan on the molecular chain can prepare a cheaper composite chitosan flocculant material and this composite chitosan flocculant was planned not only to reduce flocculation cost but also to improve flocculating function, comparing with single chitosan flocculant and the traditional chemical flocculant poly (aluminium chloride).

The objective of this work was to prepare a natural polysaccharides derivative flocculant and to examine its properties for flocculation. This flocculant product was first synthesized in our laboratory by cationic starch crosslinked with chitosan, which should result in a biodegradable flocculant product with polysaccharides backbone.

2. Materials and methods

2.1. Materials

Corn starch was obtained from Wenxing starch Co., Ltd., China; chitosan with a molecular weight of 5.2×10^5 and deacetylation degree of 95% was purchased from Yuhuan Ocean Biochemical Ltd., China. Kaolin was purchased from Sanhe Kaolin Ltd., China. Double distilled water was used throughout the experiments. Sodium hydroxide, trimethylamine, potassium dichromate, ammonium ferrous sulfate and acetic acid were purchased from Shanghai Chemical Reagent Co., China. Polyacrylamide (mean molecular weight 5×10^6) was obtained from Shanghai Chemical Reagent Co., China.

2.2. Synthesis of cationic starch with microwave-assisted method

Cat St (cationic starch) was prepared by reacting starch with 2,3-epoxypropyltrimethylammonium chloride in presence of sodium hydroxide under the condition of microwave irradiation. The Cat St obtained was washed with 80% ethanol aqueous solution until no

Cl^- was found, which was detected by silver nitrate, and then dried in a vacuum oven at $50^\circ C$ for 4 h. The nitrogen content of cationic starch was estimated using the Kjeldahl method and the degree of substitution (DS) was calculated from nitrogen content [21]:

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

N is the Kjeldahl nitrogen %. The DS of Cat St synthesized in this experiment was 0.31.

2.3. Preparation of flocculant (CATCS)

Cat St dispersed in the distilled water and chitosan dissolved in 1% acetic acid solution, were mixed together in a reactor. This mixture was stirred for 15 min using a YuHua DS-2 Multi-functional stirrer. Crosslinker was then added gradually in the mixture. The investigation of optimum synthesis conditions was carried out by altering certain experimental parameters, such as dose ratios of cationic starch and chitosan (g/g), dose ratios of crosslinker and cationic starch (mL/g), the reactive temperature ($^\circ C$), and reaction time (h). The dosage of Cat St was fixed to 2 g.

2.4. FT-IR and SEM analysis

A Thermo Nicolet Fourier-transform infrared spectrometer (Model-Nexus 870 FT-IR) was used and the potassium bromide (KBr) pellet method was used for FT-IR study. The FT-IR spectra of St (starch), Cat St (cationic starch), CS (chitosan) and CATCS were shown in Fig. 1.

Scanning electron microscopy (SEM) was investigated using a scanning electron microscope (JSM-6390). Each sample was dried, followed by coating with a thin layer of gold in vacuum before examination.

2.5. Zeta potential measurement

The charge characteristics of CATCS were characterized by zeta potential (ζ). Zeta potential is not measurable directly but it can be calculated using theoretical models and an experimentally determined electrophoretic mobility or dynamic electrophoretic mobility. The most known and widely used theory for calculating zeta potential from experimental data is the one developed by Smoluchowski and it can be calculated using the following equation

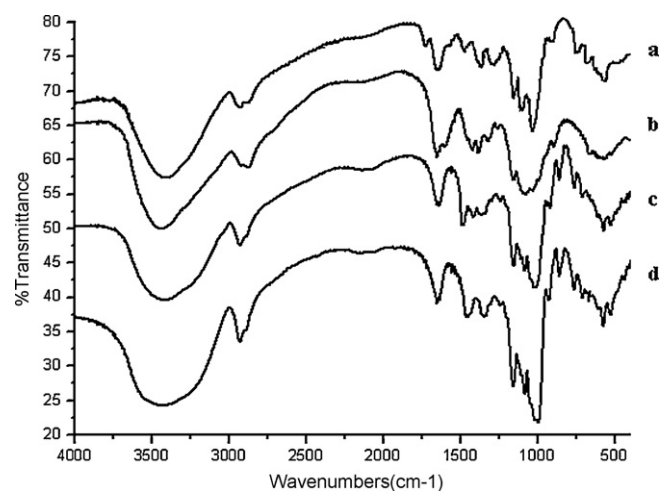


Fig. 1. FT-IR Spectrum of St (starch), Cat St (cationic starch), CS (chitosan) and CATCS: (a) FT-IR spectrum of St; (b) FT-IR spectrum of Cat St; (c) FT-IR spectrum of CS; (d) FT-IR spectrum of CATCS.

[22,23]:

$$\zeta = \frac{4\pi\eta}{\varepsilon E} \mu$$

where η is viscosity of dispersion medium, μ is electrophoresis rate, ε is the electrical permittivity, and E is the electric field.

Zeta potential is a controlling parameter of double layer repulsion for individual particles. It is corresponding to surface charge during the flocculation process [24]. The zeta potential of CATCS

was measured as described [25,26] using a DYY-8B electrophoretic analyzer and the result was 40.27 mV indicating CATCS had high positive charged [27].

2.6. Flocculation

2.6.1. Flocculation tests of kaolin suspension

5 g/L kaolin suspension prepared by mixing 5 g kaolin in 1000 mL distilled water was used for flocculation studies. The transmittance

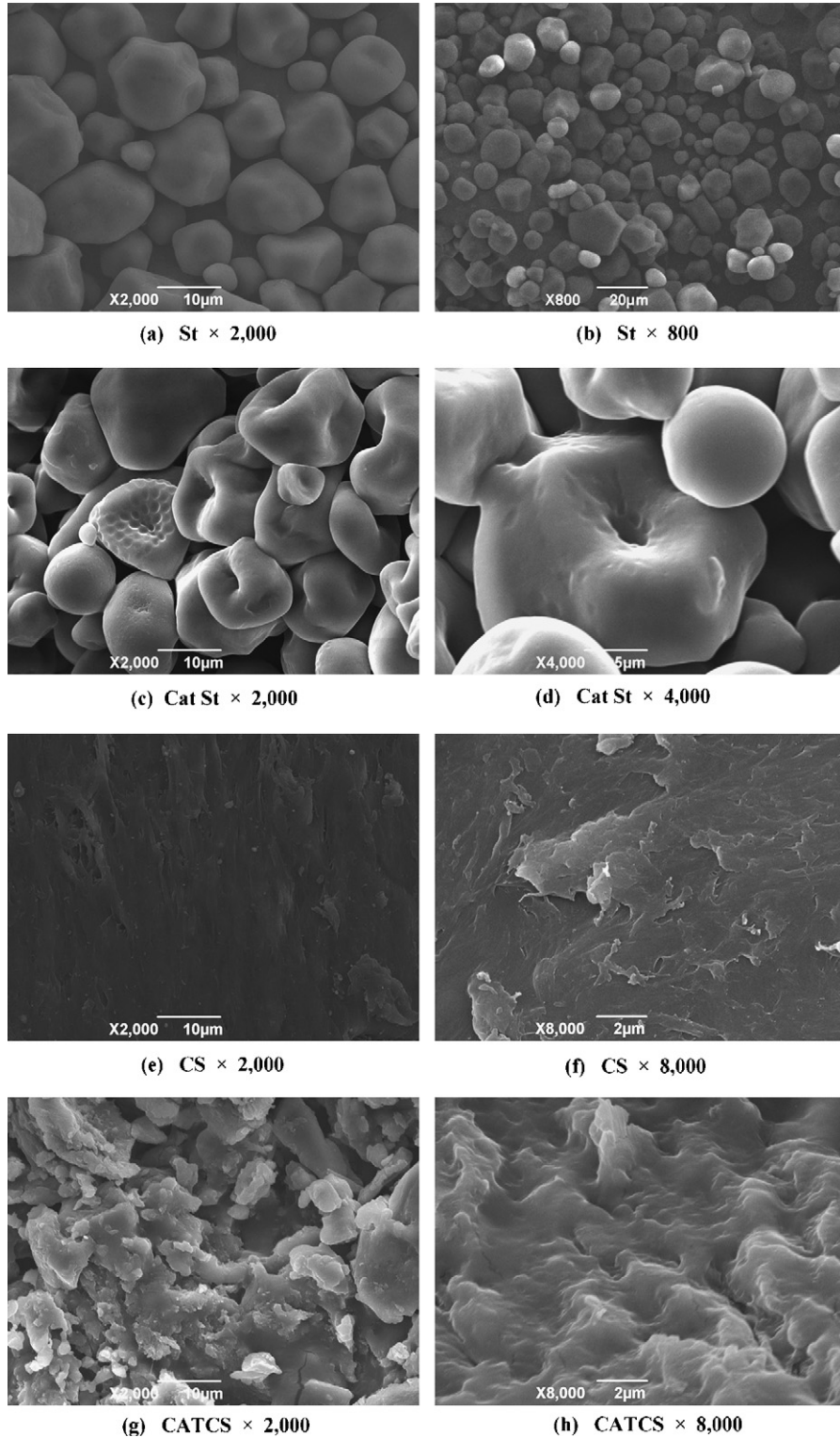


Fig. 2. SEM photos of St, Cat St, CS, and CATCS.

measurement was carried out using a Spectrumlab 22 spectrophotometer at a wavelength of 560 nm. Immediately after the addition of flocculants, the suspension was stirred at a constant speed of 150 rpm for 2 min, followed by 60 rpm for 2 min. The flocs were then allowed to settle down for 5 min. At the end of the settling period, the transmittance of the supernatant liquid was measured. The dose of flocculants was varied from 1 to 6 ppm, calculated with respect to the total weight of the solution. In this process, the flocculant performance of CATCS was compared with that of Cat St and CS in the suspension.

2.6.2. Flocculation tests of wastewater

CATCS was applied in wastewater obtained from one of sewage outlets of South Lake in Wuhan China. The parameters such as concentration of CATCS, temperature and pH effects on flocculation efficiency were discussed. Finally flocculation properties of ferric sulfate and polyacrylamide were tested as comparisons with those of CATCS. The experiments were carried out by measuring transmittance at 480 nm wavelengths and the removal rate of solid suspended particles (SS) and organic contaminant (COD) [28].

3. Results and discussions

3.1. FT-IR and SEM analysis

The FT-IR spectra of St, Cat St, CS and CATCS are shown in Fig. 1a–d, respectively.

The broad band (Fig. 1a) at 3408 cm^{-1} was due to the stretching mode of the O–H groups. An intense band at 1654 cm^{-1} was assigned to the first overtone of the O–H bending vibration. The bands at 1154 and 2929 cm^{-1} were assigned to C–O stretching and C–H stretching, respectively. Two strong bands at 1082 and 1006 cm^{-1} were attributed to $\text{CH}_2\text{--O--CH}_2$ stretching vibrations.

Fig. 1b shows the FT-IR spectrum of Cat St. the broad peak at 3414 cm^{-1} was due to the O–H stretching vibration. The two bands at 2929 and 1155 cm^{-1} were due to the C–H stretching and C–O stretching vibration, respectively. The peak at 1662 cm^{-1} was due to the first overtone of O–H bending. Two bands at 1082 and 1009 cm^{-1} were for the $\text{CH}_2\text{--O--CH}_2$ stretching vibration. The presence of an additional band at 1404 cm^{-1} assignable to the C–N stretching vibration, which was clear proof of incorporation of a cationic moiety onto the backbone of the starch.

In the case of CS (Fig. 1c), the broad peak at 3409 cm^{-1} was due to the O–H stretching vibration. 2921 cm^{-1} was due to the C–H stretching, 1954 cm^{-1} is for the characteristic absorption of --NH_2 ; the peaks at 1657 and 1594 cm^{-1} were due to the O–H and the scanty amount of O=C--NH_2 .

Fig. 1d is the FT-IR spectrum of CATCS, the absorption of new C–N–O and C–N–N bone were in the fingerprint area, which were difficulty to distinguish one by one, but it can be seen CATCS has the characteristic absorptions of Cat St (the absorption at 1409 cm^{-1} of C–N), as well as characteristic absorption of CS, because of combination between functional groups, some peaks were overlapped or enhanced.

The results of FT-IR spectrum were confirmed by SEM investigation. SEM photos of St, Cat St, CS, and CATCS were given in Fig. 2. It was obvious that the specific surface of CATCS was coarser, larger than Cat St and CS. Molecular chains of components in CATCS assembled together and had a structure of network, which could promote the absorption and bridging performance as a flocculant for water treatment.

3.2. Effect of synthesis conditions on flocculating activity of CATCS

Synthesis conditions on flocculating activity of CATCS were investigated. The flocculating activity was calculated as following

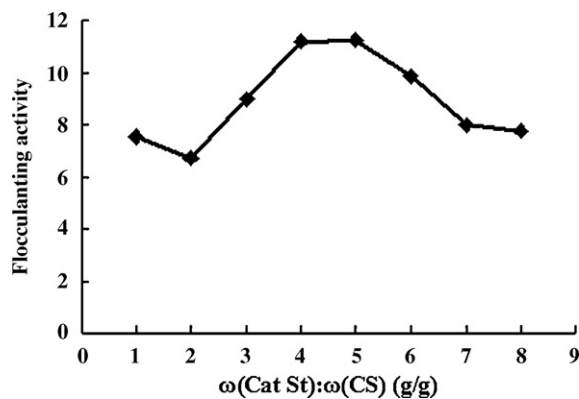


Fig. 3. Effect of mass ratios of Cat St and CS on flocculating activity.

[29]:

$$FA = \frac{1}{A_a} - \frac{1}{A_b}$$

where A_a and A_b was the absorbance of the CATCS sample and the blank sample, respectively. Dosage of CATCS was 2 mg/L for flocculation in this section.

3.2.1. Effect of mass ratio of cationic starch to chitosan on flocculating activity

The effect of ration of cationic starch to chitosan on flocculating activity was studied. Fig. 3 illustrated the effect of ω (Cat St): ω (CS) on flocculating activity of CATCS. The crosslinking temperature, dose ratio of crosslinker to crosslinking time was 50°C , 0.5 mL/g and 2.0 h , respectively. As ω (Cat St): ω (CS) increased from 1:1 to 5:1, the flocculating activity increased from 7.52 to 11.25. It indicated an appropriate ration of CS could improve the flocculating activity, but excessive mass of CS which was water insoluble, may induce decline of water solubility of CATCS and led to the decrease of flocculating activity. When it was 4:1 and 5:1, the flocculation efficiency was optimal. Due to cationic starch is much cheaper than chitosan (cationic starch is $0.31\text{--}0.87\text{ \$/kg}$ and chitosan is $11.6\text{--}43.87\text{ \$/kg}$), the ratio of 5:1 was opted.

3.2.2. Effect of dose ration of crosslinker and Cat St on flocculating activity

Fig. 4 showed the value of flocculating activity versus dose rate of crosslinker and Cat St. ω (Cat St): ω (CS), crosslinking temperature and crosslinking time were confirmed: 5:1 (g/g), 50°C , and 2.0 h , respectively.

According to Fig. 4, when ratio of crosslinker to Cat St rose from 0 to 0.75 mL/g , the value of flocculating activity increased sharply

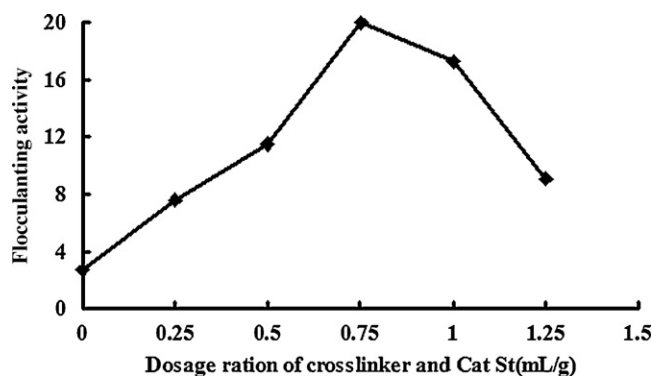


Fig. 4. Effect of dosage ration of crosslinker (mL) and Cat St (g) on flocculating activity.

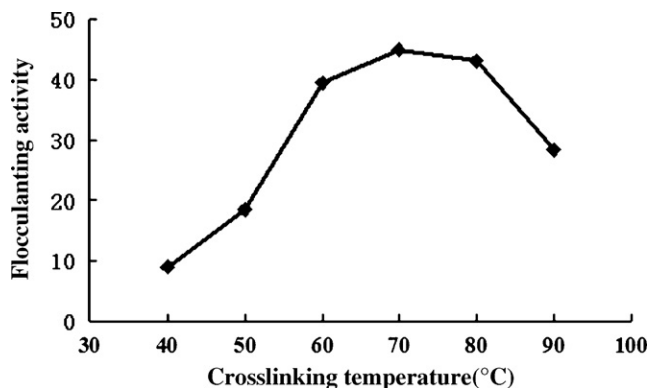


Fig. 5. Effect of crosslinking temperature on flocculating activity.

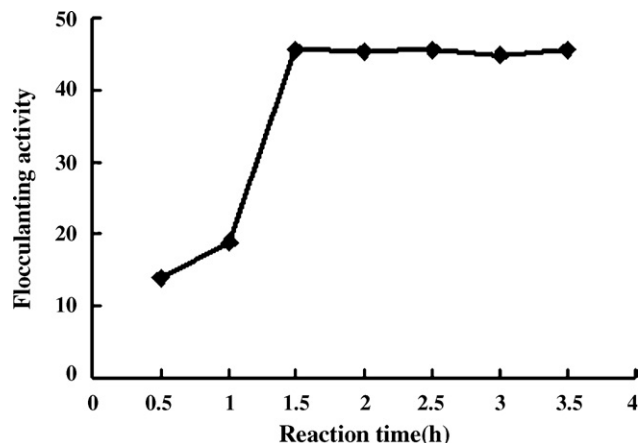


Fig. 6. Effect of reaction time on flocculating activity.

from 2.73 to 20.00. As the dose ratio of crosslinker and Cat St rose, the degree of crosslinking increased and molecule weight of CATCS increased which enhanced its bridging capability, thus flocculating activity was improved. However, when the dose ratio was more than 0.75 mL/g, the molecular weight of the flocculant became excessive and water-soluble property of CATCS became worse which made the movements of the molecular chain inactive and function groups wrapped, thus the flocculating activity declined.

3.2.3. Effect of crosslinking temperature on flocculating activity

In order to evaluate the effect of crosslinking temperature on flocculating activity, experiments were conducted at six different crosslinking temperatures. Mass rate of Cat St and CS, dose rate of crosslinker and Cat St, crosslinking time was 5:1, 0.75 mL/g and 2 h, respectively. The results were shown in Fig. 5. The flocculating activity increased as crosslinking temperature increased from 40 to 70 °C and decreased thereafter. Flocculating activity reached a peak value at the temperature of 70 °C. As reaction temperature increased, reaction efficiency was promoted, the degree of crosslinking increased and the molecule weight of CATCS enlarged as well, so flocculation properties of CATCS got more effective. The decrease in flocculating activity at high temperatures could be explained as follows: As polymer flocculants, macromolecule configurations and lengths play important roles in bridging flocculation [30] when the long-chain polymer molecules are adsorbed on the particles' surface, they tend to form loops and extend some distance from the particle surface into the aqueous phase [31]. Their ends also dangle and get adsorbed on the surface of another particle, forming a bridge between the particles, and bridging flocculation occurs. Molecular chains derived from Cat St may decompose at a high temperature [32,33]. This would bring on the breakage of molecular chain of CATCS, and bridging flocculation cannot occur by CATCS of broken molecular chains, of which macromolecule configurations and lengths could not form valid bridges between particles in the suspension.

3.2.4. Effect of reaction time on flocculating activity

The flocculating activity at various reaction times for the synthesis of CATCS was shown in Fig. 6. As other factors were constant (mass ratio of Cat St and CS, dose rate of crosslinker and Cat St, crosslinking time, respectively, was 5:1, 0.75 mL/g, 70 °C), reaction time varied from 0.5 to 3.5 h. It indicated that when the reaction time was in the range of 0.5–1.5 h, it had a significant effect on flocculating activity. The reaction efficiency reached a peak value in 1.5 h. With the extension of reaction time, crosslinking between the reactants increased and the molecular weight of the product got larger continuously until the reaction reached its limits by causing the reduction of reactants the greater the weight. Thus, the floccu-

lating activity reached maximum when reaction time prolonged to 1.5 h, then kept peg value thereafter.

3.3. Comparison study of flocculation performance of Cat St, CS and CATCS in kaolin suspension

The flocculation performances of Cat St, CS and CATCS in 5 g/L kaolin suspensions were studied. The results were illustrated in Fig. 7. Flocculating efficiency of CATCS increased as CATCS concentrations increased from 1 to 4 mg/L and decreased thereafter. The peak flocculating efficiency of 98% transmittance occurred at a CATCS concentration of 4 mg/L. It indicated flocculation efficiency of 2 mg/L CATCS was equivalent to that of 6 mg/L cationic starch as well as that of 6 mg/L chitosan.

The flocculation performances of 4 mg/L Cat St, CS and CATCS in 5 g/L kaolin suspension were compared in Fig. 8. A peak flocculation efficiency of CS occurred in 20 min and the maximal efficiency of CS was 91.8% in terms of transmittance. The greatest transmittance of 5 g/L kaolin suspensions processed by Cat St was 91.4%. The best flocculation performance of CATCS was 98%, which was 6.6% and 6.2% higher than those of Cat St and CS, respectively. Additionally, The maximum transmittance of the kaolin suspension processed by CATCS occurred in 12 min shorter than those of Cat St and CS of which peak flocculation efficiency occurred no less than 20 min. It indicated the flocculation reaction rate of CATCS was faster than those of Cat St and CS. It was obvious that CATCS provided higher flocculation performance than Cat St and CS in 5 g/L kaolin suspension than Cat St and CS.

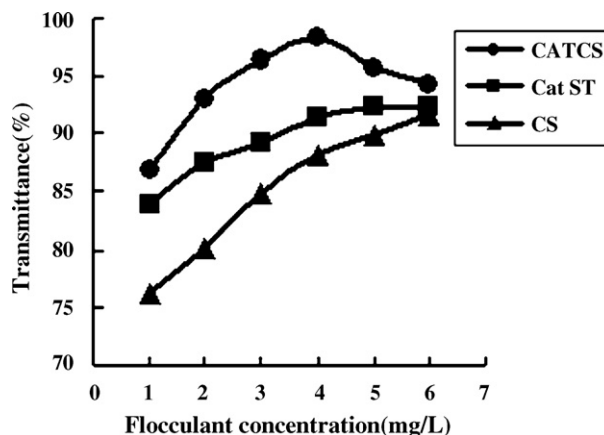


Fig. 7. Comparison of flocculation performance of Cat St, CS, and CATCS in kaolin suspension.

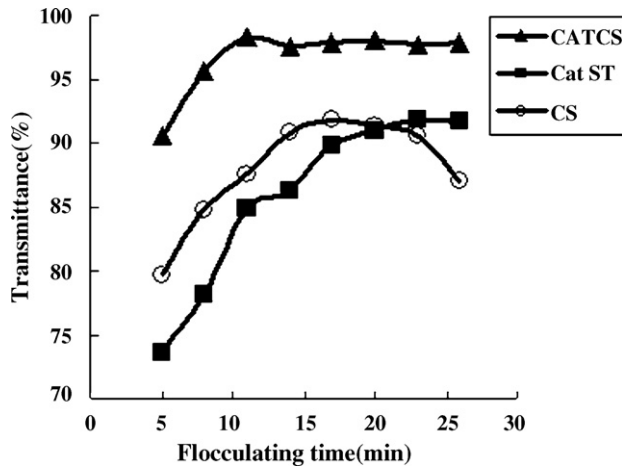


Fig. 8. Comparison of flocculation performance of CATCS in kaolin suspension. Concentration of Cat St, CS, and CATCS are all 4 mg/mL.

Table 1
Quality index of wastewater.

pH	COD (mg/L)	SS (mg/L)	Smell	Maximum absorption wavelength (nm)
7.6	551	666	Stink	480

3.4. Flocculation tests in wastewater

The wastewater used was brownish black turbid liquid, quality index of which was shown in Table 1. In this progress, influences of concentration of CATCS, temperature, and pH on flocculation efficiency of CATCS were discussed. Flocculant properties of ferric sulfate and polyacrylamide were tested as comparisons with those of CATCS under the same conditions.

3.4.1. Dosage effect on flocculation efficiency of CATCS in wastewater

The flocculation performance of a particular polymer could be evaluated by the removal of SS and COD [34]. As shown in Fig. 9, the removal rate of SS increased as the CATCS concentration increased from 1 to 4 mg/L and decreased thereafter. The removal of COD increased as the CATCS concentration increased from 1 to 6 mg/L and decreased thereafter. The removal rate of 98.6% SS and 80.17% COD was obtained at dosage of 4 and 6 mg/L, respectively. Peak removal rate of SS appeared when concentration of CATCS was in range of 4–5 mg/L, while the ultimate removal of COD occurred

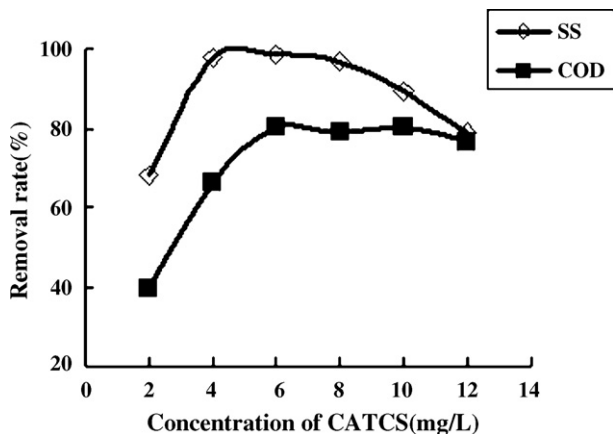


Fig. 9. Removal ration of SS and COD by different concentration of CATCS.

when dosage of CATCS was 6–10 mg/L. It indicated CATCS was not only able to aggregate inorganic and organic colloidal particles, but also absorb soluble organic substances.

On one hand, with CATCS concentration increased, removal rate of SS and COD increased, on the other, the presence of excessive polymers could restabilize particles because there would be no more vacant sites on particle surface to accept polymers that could help to form binding among particles. In addition, due to steric hindrance of polymer membrane adsorbed on the particles, aggregation of particles became difficult. Thereby, removal of SS and COD was reduced.

3.4.2. Temperature effect on flocculation efficiency of CATCS in wastewater

Flocculation reactions were carried out to inspect temperature effect on flocculation efficiency of CATCS. Fig. 10 showed that temperature had significant effect on flocculation efficiency of CATCS. Flocculation efficiency of CATCS decreased as temperature rose from 5 to 40 °C in terms of transmittance and the flocculation time to reach a maximum transmittance at a lower temperature was shorter than that at a higher one. It could be concluded that the flocculation reaction of CATCS was exothermic. CATCS had better flocculation performance at lower temperature for the wastewater and it was favorable for dealing with cool water.

3.4.3. pH effect on flocculation efficiency of CATCS in wastewater

pH had significant effects on zeta potential and surface properties of colloidal particles and flocculant agents [2]. In this experiment we investigated the effect of pH (varying from 4 to 11) on flocculation effect of CATCS while other factors were constant (CATCS dosage was 3 mg/L, temperature was 25 °C). Fig. 11 plots the transmittance against flocculation time of wasted water at various pH. It showed that excellent flocculation performance could be observed around pH 5–4 and pH 10–11, and a minimum at pH 6. The findings suggested that CATCS tends to perform better in acid and

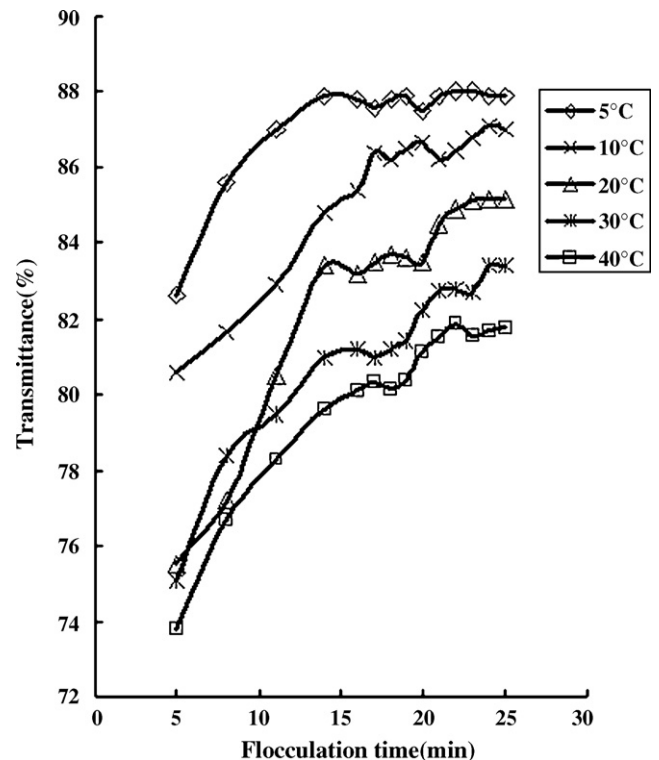


Fig. 10. Flocculation efficiency of CATCS at various temperature.

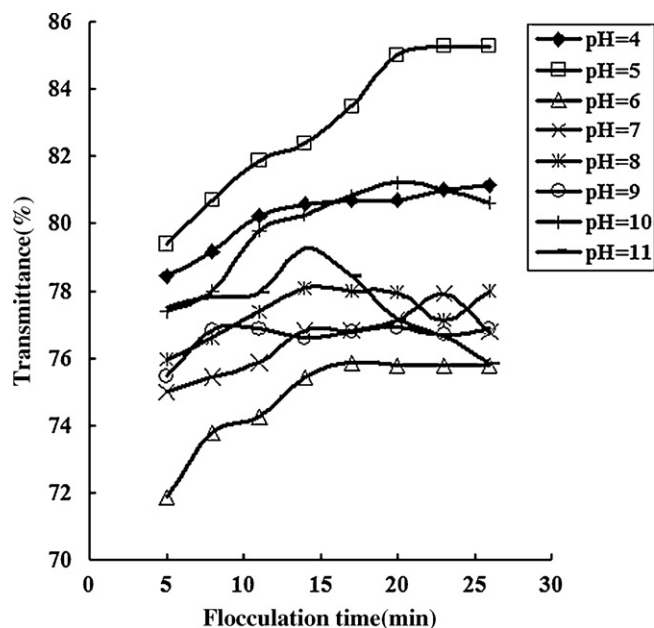


Fig. 11. Flocculation properties of CATCS at various pH.

alkaline environment as a flocculant. This was probably due to the effects of pH on surface charge and surface properties of colloidal particles and positive charged characteristic of CATCS characterized in section 2.5. pH in acid and alkaline may leads to surface charge screening and, consequently, and cause the decrease of electrostatic repulsion between particles, that in its turn allows attracting in the broader concentration range of flocculant, what was similar to the function of electrolyte predicted by DLVO theory [27].

3.5. Comparison of the flocculation performance between ferric sulfate, polyacrylamide and CATCS

The comparison of the flocculation performance between ferric sulfate, PAM and CATCS for waster were investigated. The results were showed in Tables 2–4, respectively.

Table 2 indicated that, the removal rate of COD raised from 61.2% to 80.24% with concentration of ferric sulfate varied from 20 to 120 mg/L. PAM has good properties of extension, anti-interference and flocculation in wastewater, so it is considered to be a strong and effective flocculant [5]. According to Table 3, as the PAM dosage increased, the removal rate of COD increased and a peak value of 81.01% occurred when it was 12 mg/L. Table 4 shows the trend of changing the removal rate of COD with amount of CATCS, which is similar to that of PAM. According to comparative analysis of

Table 2
Removal rate of COD_{Cr} by ferric sulfate.

Amount of ferric sulfate (mg/L)	20	40	60	80	100	120
Removal rate of COD _{Cr} (%)	61.12	65.73	71.57	75.39	78.33	80.24

Table 3
Removal rate of COD_{Cr} by PAM.

Amount of PAM (mg/L)	4	6	8	10	12	14
Removal rate of COD _{Cr} (%)	53.19	79.41	78.31	79.79	81.01	76.19

Table 4
Removal rate of COD_{Cr} by CATCS.

Amount of CATCS (mg/L)	4	6	8	10	12	14
Removal rate of COD _{Cr} (%)	66.08	80.17	78.79	80.21	76.34	63.98

Tables 2–4, removal rates of COD 6–10 mg/L CATCS were equal with those of 100–120 mg/L ferric sulfate and 8–12 mg/L PAM. To achieve the same removal rates of COD, the dosage of CATCS was only tenth dosage of ferric sulfate and its flocculation performance was similar to that of PAM with mean molecular weight of 5×10^6 .

4. Conclusion

1. A novel flocculant CATCS with high flocculation performance based on natural polymers starch and chitosan was first prepared in our laboratory. The optimal synthetic condition was confirmed: crosslinking temperature was 70 °C; ω (Cat St): ω (CS) was 5:1; the ration of crosslinker and cationic starch was 0.75 mL/g and reaction time was 1.5 h.
2. CATCS which was positive charged, trended to perform well in acidic and alkaline solution, especially in acidic solution.
3. CATCS had better flocculation performance at lower temperature for the wastewater investigated. It was favorable for dealing with cool water.
4. Flocculation behaviors and properties of CATCS are much better than those of cationic starch and chitosan for 5 g/L kaolin suspension. For the waster water investigated, the flocculation performances of CATCS were apparently over those of $\text{Fe}_2(\text{SO}_4)_3$ and similar to those PAM which is considered to be a strong and effective flocculant.

References

- [1] Yuping Wei, Fa Cheng, Hui Zheng, Synthesis and flocculating properties of cationic starch derivatives, *Carbohydr. Polym.* 74 (2008) 673–679.
- [2] W.W. Li, W.Z. Zhou, Y.Z. Zhang, J. Wang, X.B. Zhu, Flocculation behavior and mechanism of an exopolysaccharide from the deep-sea psychrophilic bacterium *Pseudoalteromonas* sp. SM9913, *Bioresour. Technol.* 99 (2008) 6893–6899.
- [3] W.A. Banks, M.L. Niehoff, D. Drago, P. Zatta, Aluminum complexing enhances amyloid (protein penetration of blood–brain barrier, *Brain Res.* 1116 (2006) 215–221.
- [4] S. Polizzi, E. Pira, M. Ferrara, M. Buginani, A. Papaleo, R. Albera, S. Palmi, Neurotoxic effects of aluminum among foundry workers and Alzheimer's disease, *Neurotoxicology* 23 (2002) 761–774.
- [5] I.L. Shih, Y.T. Van, L.C. Yeh, H.G. Lin, Y.N. Chang, Production of a biopolymer flocculant from *Bacillus licheniformis* and its flocculation properties, *Bioresour. Technol.* 78 (2001) 267–272.
- [6] M.S. Semsar, S. Scholz, W.M. Kulicke, Cationic starches as substitute for synthetic cationic flocculants in solid–liquid separation of harbor sludge, *J. Phys. Chem. B* 111 (2007) 8641–8648.
- [7] Roger Nyström, Gun Hedström, Jan Gustafsson, Jarl B. Rosenholm, Mixtures of cationic starch and anionic polyacrylate used 8for flocculation of calcium carbonate–influence of electrolytes, *Colloids Surf. A: Physicochem. Eng. Aspects* 234 (2004) 85–93.
- [8] X.X. Guo, F.Z. Shu, Z.J. Ben, Z.Y. Jin, Microwave-assisted synthesis of starch maleate by dry method, *Starch/Starke* 58 (2006) 464–467.
- [9] A.N. Jyothia, K.N. Rajasekharanb, S.N. Moorthya, J. Sreekumara, Microwave-assisted synthesis and characterization of succinate derivatives of cassava (*Manihot esculenta* Crantz) starch, *Starch/Starke* 57 (2005) 556–563.
- [10] R. Nyström, K. Backfolk, J.B. Rosenholm, K. Nurmi, Flocculation of calcite dispersions induced by the adsorption of highly cationic starch, *Colloids Surf. A: Physicochem. Eng. Aspects* 219 (2003) 55–66.
- [11] S. Pal, D. Mal, R.P. Singh, Cationic starch: an effective flocculating agent, *Carbohydr. Polym.* 59 (2005) 417–423.
- [12] V. Singh, A. Tiwari, Microwave-accelerated methylation of starch, *Carbohydr. Res.* 343 (2008) 151–154.
- [13] Svetlana Bratskaya, Simona Schwarz, Tim Liebert, Thomas Heinze, Starch derivatives of high degree of functionalization 10. Flocculation of kaolin dispersions, *Colloids Surf. A: Physicochem. Eng. Aspects* 254 (2005) 75–80.
- [14] Rachel Auzeily-Velty, Marguerite Rinaudo, Synthesis of starch derivatives with labile cationic groups, *Int. J. Biol. Macromol.* 31 (2003) 123–129.
- [15] Jian-Ping Wang, Yong-Zhen Chen, Xue-Wu Ge, Han-Qing Yu, Gamma radiation-induced grafting of a cationic monomer onto chitosan as a flocculant, *Chemosphere* 66 (2007) 1752–1757.
- [16] Y.C. Chung, H.L. Wang, Y.M. Chen, S.L. Li, Effect of abiotic factors on the antibacterial activity of chitosan against waterborne pathogens, *Bioresour. Technol.* 88 (2003) 179–184.
- [17] Zhong-Biao Wu, Wei-Min Ni, Bao-Hong Guan, Application of chitosan as flocculant for coprecipitation of Mn(II) and suspended solids from dual-alkali FGD regenerating process, *J. Hazard. Mater.* 152 (2008) 757–764.

- [18] Defang Zeng, Juanjuan Wu, John F. Kennedy, Application of a chitosan flocculant to water treatment, *Carbohydr. Polym.* 71 (2008) 135–139.
- [19] C.P. Huang, S.C. Chen, J.R. Pan, Optimal condition for modification of chitosan: a biopolymer for coagulation of colloidal particles, *Water Res.* 34 (2000) 1057–1062.
- [20] S. Wibowo, G. Velazquez, V. Savant, J.A. Torres, Effect of chitosan type on protein and water recovery efficiency from surimi wash water treated with chitosan–alginate complexes, *Bioresour. Technol.* 98 (2005) 539–545.
- [21] Dalia Sableviciene, Rima Klimaviciute, Flocculation properties of high-substituted cationic starches, *Colloids Surf.* 259 (2005) 23–30.
- [22] A.V. Delgado, F. Gonzalez-Caballero, R.J. Hunter, L.K. Koopal, J. Lyklema, Measurement and interpretation of electrokinetic phenomena (IUPAC technical report), *Pure Appl. Chem.* 77 (10) (2005) 1753–1850.
- [23] B.J. Kirby, E.F. Hasselbrink Jr., Zeta potential of microfluidic substrates: 2. Data for polymers, *Electrophoresis* 25 (2004) 203–213.
- [24] M.G. Rasteiro, F.A.P. Garcia, P. Ferreira, A. Blanco, C. Negro, E. Antunes, The use of LDS as a tool to evaluate flocculation mechanisms, *Chem. Eng. Processing* 47 (2008) 1323–1332.
- [25] H.C. van der Mei, A.J. Léonard, A.H. Weerkamp, P.G. Rouxhet, H.J. Busscher, Properties of oral streptococci relevant for adherence: zeta potential, surface free energy and elemental composition, *Colloids Surf.* 32 (1988) 2462–2466.
- [26] M.M. Cowan, H.C. Van der Mei, I. Stokroos, H.J. Busscher, Heterogeneity of surfaces of subgingival bacteria as detected by zeta potential measurements, *J. Dent. Res.* 71 (1992) 1803–1806.
- [27] S. Wall, P. Samuelsson, G. Degerman, P. Skolund, A. Samuelsson, The kinetics of heteroflocculation in the system cationic starch and colloidal anionic silicic acid, *Colloid Interf. Sci.* 151 (1992) 178–188.
- [28] H. Ishii, M. Koyama, T. Mitani, Removal of organic acids by highly swollen chitosan beads. Soluble polymer in water purification, *Environ. Sci. Health (Part A)* 5 (1995) 945–950.
- [29] P. Prasertsan, W. Dermlim, H. Doelle, J.F. Kennedy, Screening, characterization and flocculating property of carbohydrate polymer from newly isolated *Enterobacter cloacae* WD7, *Carbohydr. Polym.* 66 (2006) 289–297.
- [30] S. Stoll, J. BuZe, Computer simulation of bridging flocculation processes: the role of colloid to polymer concentration ratio on aggregation kinetics, *J. Colloid Interf. Sci.* 180 (1996) 548–563.
- [31] R.P. Singh, T. Tripathy, G.P. Karmakar, Novel biodegradable flocculants based on polysaccharides, *Curr. Sci.* 78 (2000) 798–803.
- [32] Pi-xin Wang, Xiu-li Wu, Xue Dong-hua, Xu Kun, Tan Ying, Du Xi-bing, Li Wen-bo, Preparation and characterization of cationic corn starch with a high degree of substitution in dioxane–THF–water media, *Carbohydr. Res.* 344 (2009) 851–855.
- [33] R. Kavaliauskaite, R. Klimaviciute, A. Zemaitaitis, Factors influencing production of cationic starches, *Carbohydr. Polym.* 73 (2008) 665–675.
- [34] Q.Y. Yue, B.Y. Gao, Y. Wang, H. Zhang, X. Sun, S.G. Wang, R.Gu. Roy, Synthesis of polyamine flocculants and their potential use in treating dye wastewater, *J. Hazard. Mater.* 152 (2008) 221–227.