

Synthesis, Characterization, and Properties of Polymeric Flocculant with the Function of Trapping Heavy Metal Ions

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Received 6 September 2007; accepted 19 June 2008

DOI 10.1002/app.29243

Published online 22 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel crosslinked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) was synthesized by grafting copolymerization reactions of crosslinked corn starch, acrylamide (AM), and sodium xanthate, using epichlorohydrin (EPI) as crosslinking reagent and ceric ammonium nitrate as initiator in aqueous solution. The effects of some factors, such as crosslinker, initiator, AM, NaOH and so forth, on the flocculation were investigated in terms of efficiency of grafting (% GE), grafting percentage (% GP), and viscosity averaged molecular weight (*M*) of the PAM pendant chains. The results showed that the CSAX was successfully synthesized with

the different number and length of grafted PAM pendant chains and with the functions of removing both substance causing turbidity and heavy metal ions from aqueous solution. Under optimum synthesis conditions, CSAX exhibited excellent performances: the rate of turbidity removal (% *T*) reached 98.4% and the rate of Cu²⁺ removal (% *R*) reached 99.2% in water treatment, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 135–141, 2009

Key words: flocculation; trapping heavy metal; crosslinked starch; graft copolymerization; xanthation

INTRODUCTION

Starch is cheap, renewable, biodegradable, and the most abundant organic raw material. It has a capacity to acquire properties significantly extending its possible applications in food and nonfood industrial sectors as a result of physical and chemical modification.^{1,2} One of the applications of starch derivatives is acting as flocculants. For example, Aerofloc (American Cyanamid Corp.), Budond (American Buckman Corp.), Zfloc-Aid, Starches 613-45 and Zyork Shiree (National Starch and Chemical Corp.), Wisprofloc (Britain Yorkshire Dye Corp.), and so on,³ are all polyvalent flocculants of starch derivatives in the world. During preparing these medicaments for water treatment, there are often three methods: crosslinking, graft copolymerization, and esterification.

Crosslinking starch with Epichlorohydrin (EPI) is the most common method used in preparation of polysaccharide-based derivatives. Glycerol monoether is formed by hydroxy group of starch and EPI, which makes molecules of starch bridged together

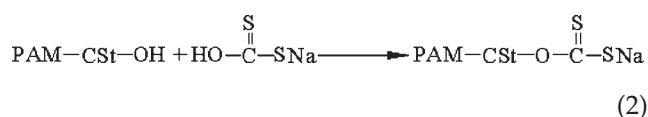
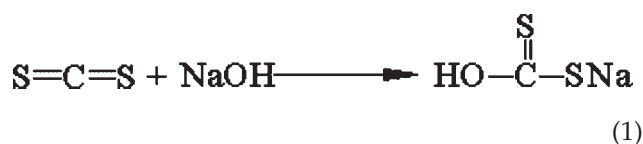
and come into being three-dimensional space-net structures. Franck et al.^{4,5} have studied this reaction using FTIR, elemental analysis, electrophoretic mobility, and NMR spectroscopy techniques in detail. The results showed that the extent of crosslinking be calculated on basis of total EPI introduced into the reaction mixture or qualitatively determined from the physical behavior of the crosslinked starch products.⁶ In this work, crosslinking of starch was employed to make the flocs formed by the products separate from the aqueous phase fleetly and effectively.

Many graft copolymers have been synthesized by grafting polyacrylamide (PAM) onto starch derivatives, and different initiators to initiate grafting PAM onto starch have been studied. The formations of free radicals on the backbone polymer by cerium have been also demonstrated by electron spin resonance.⁷ The loci of initiation of polymer formation on the starch backbone polymer are radicals formed by the oxidative reactions of ceric ions with starch chain ends containing hemiacetal linkages, glycol linkages leading to C₂–C₃ bond cleavage.⁸ It has been observed that the graft copolymers with less but longer PAM branches exhibit better flocculation characteristics. It was postulated by Rath and Singh⁹ that graft copolymers are more effective compared

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with the linear polymers because of their greater approachability to the contaminants. In another study, the similar results were obtained by Rath and Singh⁹ via comparing the flocculation behavior of St-g-PAM and Amylopectin-g-PAM.

CS₂ reacts with alkali to form xanthogenate [eq. (1)]. Then xanthogenate combines with starch or its derivatives and thus starch-xanthogenate is formed, which is known as xanthation [eq. (2)].^{10,11} The corresponding reactions are as follows:



Like the reactions between sodium sulfide and heavy metals, the heavy metal ions react with CSS groups to form metal-xanthate complexes. According to the solubility of starch xanthates before reacting with metal ions they are classified as two types: water-soluble starch xanthates (SSX) and water-insoluble starch xanthates (ISX). One of the major limitations of the SSX process is the separation of the metal-starch xanthate precipitate complex from the aqueous phase.^{12,13} Compared with SSX, ISX with the low solubility product (K_{sp}) values and high stability constants of metal-ISX that has been reported to be an effective method for heavy metal removal from aqueous solutions.¹⁴⁻¹⁸ However, insolubility of ISX results in large tonnage use of it in service; this is a hard problem as flocculant.

In view of the information just presented, in our work several attempts have been made to combine the best properties of both by copolymerization and xanthation with crosslinked starch (CSt). A synthetic method was developed to introduce PAM graft chains and the strong ligand CSS into CSt simultaneously and to obtain a new flocculant cross-linked starch-*graft*-polyacrylamide-*co*-sodium xanthate (CSAX). Owing to the molecule of CSAX containing both water-insoluble CSt and water-soluble PAM, it is semisoluble state that is easier to make the wastewater destabilize by CSAX than by SSX, and also the dosage of CSAX was less than that of ISX. Because CSAX is able to remove turbidity by bridging flocculation and dissolved metal ions by complex formation with the CSS groups and the $-\text{COO}^-$ groups generated by hydrolyzation of $-\text{CONH}_2$ together. Therefore, it is possible to reduce the subsequent units in wastewater treatment.

EXPERIMENTS

Materials

Corn starch (Food grade) was supplied by packing-house, China. α -amylase was from Xiasheng Corp., Ningxia, China. Acrylamide (AR, Shanghai Chemical Reagent Factory, Shanghai, China) and ceric ammonium nitrate (CAN) (AR, Beijing Chemical Reagent Corp., Beijing, China) were used as graft monomer and initiator, respectively. Kaolin, epichlorohydrin (EPI), acetone (AR, Tientsin Chemical Reagent Factory, Tientsin, China), and other compounds were used as purchased. All solutions were prepared with distilled water.

Synthesis and characterization of CSt

Corn starch (50 g) and 1% (w/v) sodium chloride solution (75 mL) were put into a 250-mL three-necked flask equipped with a stirrer and a thermometer.¹⁹⁻²² The slurry was heated to 30°C and kept at a constant temperature in water bath. KOH solution (15%, w/v; 20 mL) was added to this slurry, and then EPI was added dropwise for about 5 min. After 8 h, the reaction was completed. The CSt suspension slurry was adjusted to pH 7.0 with 1 mol/L HCl and 1 mol/L NaOH solution, and then the filtered solid was washed successively with distilled water (100 mL) and several portions of ethanol (100 mL total). After drying in a vacuum oven at 60°C to a constant weight, the CSt was milled and screened.

Dried CSt (10 g) was treated with 100 mL of distilled water to prepare uniform slurry, which was stirred and heated to 85–90°C, and then kept at a constant temperature for 20 min. After cooling to room temperature, it was decanted into graduated flask (100 mL) and kept at constant volume with distilled water settled for 24 h, and the volume of precipitate was named as settling volume (SV).²³

Synthesis and characterization of crosslinked starch-*graft*-polyacrylamide

A series of the CSA were prepared by using different amounts of initiator, CSt, and AM according to the following procedure: CSt (2 g) was treated with 20 mL distilled water to prepare uniform slurry, and then different concentration of AM solution (40 mL) was added. The mixture was placed in a 250-mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a gas inlet system. The flask was immersed in a water bath and heated to 45°C under nitrogen. After 15 min, CAN was added. The polymerization was continued under constant stirring and in a nitrogen atmosphere for 3 h. Then the mixture was cooled to room temperature,²⁴

precipitated in acetone, and filtered. The crude products dried in a vacuum oven at 60°C.

The crude products of CSA were extracted by Soxhlet extractor. Mixture solutions of glycol and acetic acid (40 : 60, v/v) were used as solvent. The purified CSA was precipitated in acetone and then was dried in a vacuum oven to constant weight at 60°C. The efficiency of grafting (% GE)^{25,26} and grafting percentage (% GP)²⁷ were calculated as follows:

$$\% \text{ GE} = 100(W_2 - W_1)/W_3 \quad (3)$$

$$\% \text{ GP} = 100(W_2 - W_1)/W_2 \quad (4)$$

where W_1 , W_2 , and W_3 are the weights of pure starch, graft copolymer, and AM monomer, respectively.

The intrinsic viscosity ($[\eta]$) of PAM pendant chains was determined with the help of Ubbelohde capillary viscometer. Sample of the polymer (0.1 g) was dissolved in 1 mol/L NaCl solution. From the time of flow of pure solvent (t_0 , for 1 mol/L NaCl solution) and the polymer solutions (t), relative viscosity ($\eta_r = t/t_0$) was obtained. The terms related to viscosity measurements²⁸ were given as follows: specific viscosity = $\eta_r - 1 = \eta_{sp}$; reduced viscosity = $\eta_{sp}/C = \eta_{red}$; inherent viscosity = $\ln \eta_r/C = \eta_{inh}$; and intrinsic viscosity = $(\ln \eta_{sp}/C)_{C \rightarrow 0} = [\eta]$. The intrinsic viscosity values of graft copolymer were given in Table II. The intrinsic viscosity measurement curves were shown in Figure 1.

The grafted PAM pendant chains were isolated from the CST backbone by a treatment with α -amylase. The detailed procedure was as follows: purified CSA (1 g) and α -amylase (0.002 g) were added to a 50-mL conical flask, and then 10 mL distilled water was added and stirred magnetically. The slurry was maintained at 60–65°C for 2 h. After that the mixture was filtered using sand funnel, and the obtained filtrate was poured into a large excess of acetone. The PAM recovered was purified by dissolution in warm water and precipitation in acetone. The molecular weight of the isolated PAM pendant chains was determined by viscosity measurements in an aqueous NaCl (1 mol/L) solution using the formula of Mark-Houwink:

$$M = \kappa[\eta]^\alpha \quad (1 \text{ mol/L NaCl solution, } 30 \pm 0.1^\circ\text{C}) \quad (5)$$

where the κ and α values are 802 and 1.25, respectively; $[\eta]$ is intrinsic viscosity; M is the viscosity averaged molecular weight of the PAM pendant chains.²⁸

Synthesis and characterization of CSAX

CSA (1 g) was xanthated by adding 3 mol/L NaOH (20 mL) and CS₂ (2 mL) into the sealed conical flask dropwise and stirring magnetically at 30°C in a

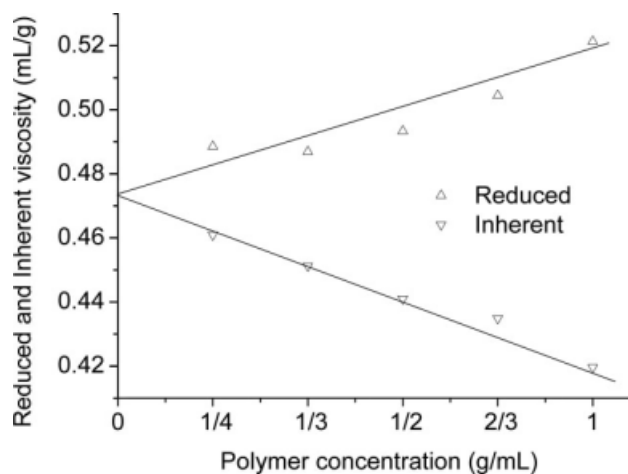


Figure 1 Intrinsic viscosity measurement of CSAX-7.

water bath for 3 h until it turned into saffron yellow. The products were cooled to room temperature, precipitated and filtered, and washed with acetone (50%) three times, pure acetone one time, dried to a constant weight at 30°C.

Turbidity removal and Cu²⁺ removal of CSAX

CSAX (10 g/L), 5% (w/v) kaolin suspension, and 10 g/L CuSO₄ solution were prepared as stock solutions.

For each test 1 L tap water, 1 mL kaolin suspension, and 3 mL CuSO₄ solution were added to a 1.5 L jar. The jars were placed on the six-joint-stirrers and agitated by stirring blades in the suspension. The different dosage of CSAX solution was added into different jars, which were stirred at uniform speed of 140 rpm for 2 min, and then at 40 rpm for 10 min. Then the precipitates were allowed to settle for 10 min and the supernatant removed. The rate of turbidity removal (% T) and the rate of Cu²⁺ removal (% R) of a water sample was measured by the turbidity meter (Hanna instruments, Italy)⁹ and 220 FS atomic absorption spectrometer (made in corp. Varian, USA), respectively, and calculated as follows:

$$\% T = 100(T_0 - T_1)/T_0 \quad \% R = 100(R_0 - R_1)/R_0 \quad (6)$$

where T_0 and T_1 are the turbidity of initial suspension and supernatant, respectively. R_0 and R_1 are the metal ions concentration of initial suspension and supernatant, respectively.

RESULTS AND DISCUSSION

Effect of EPI on the performance of CSAX

The crosslinking degree of starch is determined by the SV to study the effect of crosslinking degree of

TABLE I
Effect of EPI on the Performance of CSAX

| No. | Starch (g) | EPI (mL) | SV (mL) | T (%) | R (%) |
|-----|------------|----------|---------|-------|-------|
| 1 | 50 | 1 | 81.3 | 52.3 | 80.7 |
| 2 | 50 | 2 | 73.6 | 55.4 | 85.1 |
| 3 | 50 | 3 | 56.4 | 80.4 | 93.2 |
| 4 | 50 | 4 | 45.0 | 89.6 | 96.7 |
| 5 | 50 | 5 | 42.1 | 85.5 | 84.3 |
| 6 | 50 | 6 | 38.3 | 81.3 | 74.2 |
| 7 | 50 | 7 | 36.2 | 78.5 | 56.3 |

starch on the performances of CSAX. The preparation of CSA conditions are as follows: CSt = 2 g, [AM] = 0.939 mol/L, and [CAN] = 6.67×10^{-4} mol/L at 45°C for 3 h. The preparation of CSAX conditions are as follows: CSA = 1 g, NaOH = 20 mL (3 mol/L), CS₂ = 2 mL, at 30°C for 3 h. The flocculation of CSAX conditions are as follows: 5% (w/v) kaolin (1 mL, initial NTU = 65), 10 g/L CuSO₄ (3 mL), initial pH = 5.0 adjusted with 1 mol/L HCl and 1 mol/L NaOH solution, 1 L water sample, dosage of CSAX 70 mg/L.

Weights or volumes of reactants as well as performances of CSAX for several preparations are listed in Table I. With the increase of EPI dosage from 1 to 7 mL, the SV decreased from 81.3 to 36.2 mL. But the % T and % R increase first and decrease afterwards. There is a maximum value at No. 4. The results may be explained by the fact that the network structure of the CSAX cannot be formed efficiently, and the greater solubility of products makes solid-liquid separation difficult when the EPI is low. In contrast, a higher EPI results in the formation of more crosslinks which in turn cause the formation of a three-dimensional space-net structures and an increase in molecular weight, which decrease the swelling and solubility of products. Therefore, it is a key for the performance of CSAX that starch is crosslinked moderately. A similar observation was also reported by Liu and Corke²⁹ and Jyothi et al.³⁰

Effect of CAN and AM concentration on the performance of CSA

In synthesizing the series of grafting copolymers, the aim is to have a number of grafting copolymers with the different number and length of PAM chains. Comparing the six grafting copolymers in the Table II, the polymerization reaction does not take place if a concentration of CAN is below 1.66×10^{-4} mol/L. When the AM concentration is fixed, with the increase of CAN from 6.67×10^{-4} to 13.34×10^{-4} mol/L the % GE, % GP, $[\eta]$ and M show a downward trend. Because of the increase in CAN, the quantity of grafted polyacrylamide is increased; therefore, the % GE and % GP increase too [from eq. 3)]. By contraries, more free radical sites on CSt backbone and the formation of homopolymer possible lead to the decrease of % GE and % GP. A large number of short PAM chains come into being, which should be reflected in its low $[\eta]$ and M . Moreover a higher concentration of CAN should be result in a homopolymerization.³¹ Studying on flocculation behavior of such polymers, we find that the copolymers with less but longer chains have more effective flocculation.

Similarly, comparing CSA-4 with CSA-2 and CSA-3, we observe a sharp increased trend of % GE, % GP, $[\eta]$ and M . Here, the CAN concentration is fixed; there is the same number of free radical sites on CSt backbone. With increase in the quantities of AM, the length of PAM chains become long continually, the % GE and % GP increase too. Of course, high concentration of AM always resulted in homopolymerization; Owen and Shen³¹ have observed that [AM] < 2.0 mol/L resulted in absence of homopolymerization.

Effect of NaOH and CS₂ on the performance of CSAX

Also the NaOH and CS₂ concentration play an important role in the preparation of CSAX. The samples of CSA-7 are xanthated at different dosages of

TABLE II
Synthesis of CSA

| Polymer code | Starch (g) | Temp (°C) | Time (min) | CAN $\times 10^{-4}$ (mol/L) | AM (mol/L) | GP (%) | GE (%) | $[\eta] \times 10^{-3}$ (mL/g) | $M \times 10^{-5}$ |
|--------------|------------|-----------|------------|------------------------------|------------|--------|--------|--------------------------------|--------------------|
| CSA-1 | 2 | 45 | 180 | 1.66 | 0.470 | — | — | — | — |
| CSA-2 | 2 | 45 | 180 | 6.67 | 0.470 | 14.1 | 35.8 | 247 | 7.85 |
| CSA-3 | 2 | 45 | 180 | 6.67 | 0.705 | 53.3 | 57.1 | 295 | 9.81 |
| CSA-4 | 2 | 45 | 180 | 6.67 | 0.939 | 68.6 | 72.7 | 474 | 17.74 |
| CSA-5 | 2 | 45 | 180 | 8.30 | 0.939 | 65.4 | 67.7 | 311 | 10.48 |
| CSA-6 | 2 | 45 | 180 | 10.00 | 0.939 | 56.4 | 58.7 | 293 | 9.73 |
| CSA-7 | 2 | 45 | 180 | 13.34 | 0.939 | 52.6 | 53.5 | 263 | 8.49 |

% GP and % GE are calculated from the eq. (3); $[\eta]$ and \bar{M} are calculated from the eqs. (5) and (4), respectively.

TABLE III
Effect of NaOH and CS₂ on the Performance of CSAX

| CSAX copolymer | CSA-7 (g) | NaOH (g) | CS ₂ (mL) | Temp (°C) | Time (h) | Contents of elements (%) | | | | T (%) | R (%) |
|----------------|-----------|----------|----------------------|-----------|----------|--------------------------|------|------|------|-------|-------|
| | | | | | | C | H | N | S | | |
| CSAX-A | 2 | 1.5 | 0.6 | 30 | 3 | 24.28 | 4.73 | 2.96 | 5.42 | 95.3 | 60.4 |
| CSAX-B | 2 | 3 | 1.2 | 30 | 3 | 23.97 | 4.45 | 2.76 | 6.45 | 96 | 78.6 |
| CSAX-C | 2 | 4.5 | 1.8 | 30 | 3 | 23.69 | 3.98 | 2.66 | 6.88 | 97 | 90.9 |
| CSAX-D | 2 | 6 | 2.4 | 30 | 3 | 23.03 | 3.88 | 2.59 | 7.41 | 98.4 | 99.0 |
| CSAX-E | 2 | 7.5 | 3.0 | 30 | 3 | 22.89 | 3.84 | 2.16 | 7.41 | 96 | 99.0 |

NaOH and CS₂. First the molar ratio of NaOH to CS₂ is fixed at 4 : 1, and then the dosages of NaOH and CS₂ are changed. The flocculation conditions are as follows: 5% (w/v) kaolin (1 mL, initial NTU = 65), 10 g/L CuSO₄ (3 mL), initial pH 5.0 adjusted with 1 mol/L HCl and 1 mol/L NaOH solution, 1 L water sample, the dose of CSAX 70 mg/L. The results are shown in Table III.

It can be seen that the *S* % (the percentage of sulfur of CSAX), % *T*, and % *R* increase from 5.42, 85.3, and 60.4% to 7.41, 90.6, and 99.0%, when the quantities of NaOH and CS₂ are raised from 1.5 g and 0.6 mL to 6 g and 2.4 mL, respectively. This may be due to an enhanced conversion of CS₂ which result in an increasing number of xanthate groups on CSt. A further increase in the quantity of NaOH and CS₂ do not find obvious changes of % *S* and % *R*, whereas the % *T* slowly decreases. Because the CSAX removes heavy metal ions by chelation,³² when the % *S* remains invariable, the amount of =CSS⁻ groups of CSAX is constant, and the % *R* remains constant too. The decrease in % *T* may be ascribed to the excessive hydrolyzation of PAM pendant chains. The produced -COO⁻ groups increase the negative charge of CSAX. The -COO⁻ and =CSS⁻ groups result in repulsion between flocculant and contaminant particles with negative charge, which does not favor flocculation.

culant and contaminant particles with negative charge, which does not favor flocculation.

Flocculation characteristics of CSAX

The flocculation study is carried out using three types of starch derivatives, namely, CSAX-1, 2, and 4, which prepare with CSA-1, 2, and 4 by xanthation, respectively. The prepared conditions are as follows: CSA = 2 g, NaOH = 6 g, CS₂ = 2.4 mL, at 30°C for 3 h. The flocculation conditions are as follows: 5% (w/v) kaolin (1 mL), 10 g/L CuSO₄ (3 mL), initial pH 5.0 adjusted with 1 mol/L HCl and 1 mol/L NaOH solution, 1 L water sample. Here, CSAX-1, 2, and 4 is deliberately chosen from among the seven graft copolymers because CSAX-1 has no grafting PAM chains as well as CSAX-2 and CSAX-4 has different number and length of PAM chains. The results of the % *T* and % *R* are shown in Figures 2 and 3.

Mechanism of removal turbidity and Cu²⁺

Flocculation are used to optimize the separation of a solid phase from the liquid phase in aqueous suspensions with polyelectrolytes (cationic, anionic, or ampholytic) mainly by a bridging,³³ doublelayer

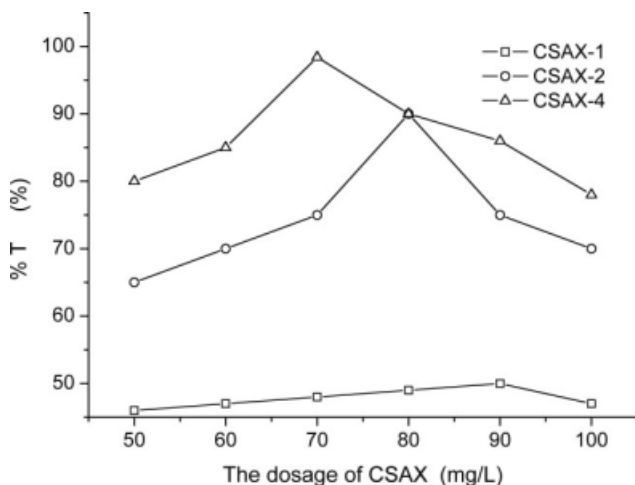


Figure 2 The relationship between the dosage of CSAX and % *T*.

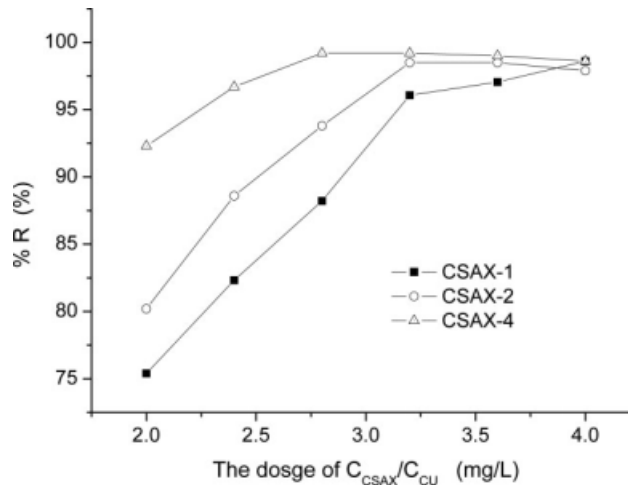
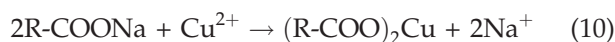
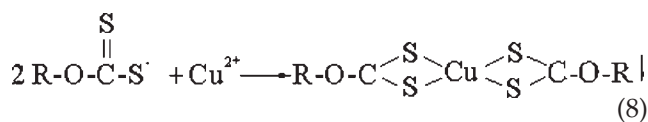
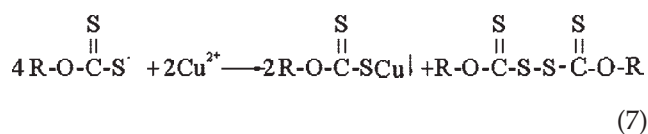


Figure 3 The relationship between the dosage of CCSAX/CCu and % *R*.

compression,³² electric neutralization,³⁴ sweep flocculation mechanism,³⁵ and so forth. According to the above investigation, CSAX loads negative charge. Thus the suspended particles are aggregated with CSAX mainly by a bridging and sweep mechanism. CSAX with the length of the polymer chain is crucial for effective bridging to occur. The longer the chains (high molecular weight) have, the greater the chances of interacting with more than one particle are.²⁸ CSAX reacts with Cu^{2+} to form a Cu-CSAX complex precipitate, which entrains fine particles of other suspended solids as it settles in sweep flocculation.³⁶ Depending on the structure of CSAX containing a larger of polar groups, removal Cu^{2+} can be obtained by several mechanisms such as physical adsorption, ion exchange, electric neutralization, and chelation. For example, $=\text{COO}^-$ groups react with Cu^{2+} by chelation to form Cu-CSAX chelate, and $-\text{COO}^-$ groups react with Cu^{2+} by ion-exchange to form complex. The coordination groups chelating one and the same metal ion maybe come from the different CSAX molecules. The formation structure with higher crosslinking degree and spatial structure have a better flocculation to make them settle speedily. For oxidative heavy metal ions (i.e., Cu^{2+} , Fe^{3+} , CrO_4^{2-} , etc.), the reactions are not only chelation but also oxidation-reduction. The route could potentially take place according to eqs. (7)–(10)³⁷



Effect of different type of CSAX on % *T*

Figure 2 shows the plot of % *T* versus the dosage of CSAX. It is apparent that with increase in the dosages up to a certain level, the % *T* increases and then a decreasing trend was observed with further increase in dosage level. The orders of % *T* of CSAX are CSAX-4 > CSAX-2 > CSAX-1. This can be reasonably explained as follows: Polymer bridging plays a large part in the flocculation process. CSAX-1 has no grafting PAM chains, and can not bring bridging flocculation. The % *T* of CSAX-1 may be formed by sweep flocculation only, therefore the flocculation is the lowest. With the present of a large

number of short grafting PAM chains, CSAX-2 with the original compact shape will not alter to a great extent, thus retaining its lower performance of flocculation, which should be reflected again in its low $[\eta]$. While fewer and longer of PAM chains of CSAX-4, which goes beyond the distance formed by electrostatic repulsion between contamination particles, result in optimal bridging flocculation. The difference value of % *T* of CSAX-1, 2, and 4 at the same dosage maybe reflect the extent of bridging flocculation. As a result, the longer PAM chains are, the better bridging flocculation has. The optimal dosage is first reached at 70 mg/L. Further increase the dosage of CSAX result in the decline of % *T*. This result may be ascribed to restabilization of water sample on the overdosing of the CSAX, which make the lost bridging gradually.

Effect of different type of CSAX on % *R*

The effect of different types of CSAX on % *R* is shown in Figure 3. In all the cases, as the dosages of CSAX increase, the % *R* increases up to the maximum and then slowly decreases. CSAX-4 first reaches the optimum value of % *R* followed by CSAX-2 and CSAX-1. It is well known that the performances of polymers are significantly influenced by the structure of the polymer in solution.³⁸ From the section "effect of different type of CSAX on % *T*," it is clear that CSAX-4 with less and longer PAM chains has large hydrodynamic volume, whereas CSAX-2 with more and short PAM chains retains lower hydrodynamic volume. After the hydrolyzation, it is enough exposed that the effective functional groups on CSAX-4. From Table II, the % GE and % GP of CSA-4 are 72.7 and 68.6%, whereas the % GE and % GP of CSA-1, 2 are 0, 35.8% and 0, 14.1%, respectively. Here CSAX-1, 2, and 4 are xanthated at the same conditions. So, the quantities of $-\text{COO}^-$ on CSAX-4 is more than that of CSAX-2, it is feasible that the more Cu^{2+} are removed by ion-exchange reaction [eqs. (9) and (10)]. In Figure 3, the difference value of % *R* of CSAX-1, 2, and 4 represents Cu^{2+} removed by ion-exchange reaction at the same dosage. Further increases in the dosage of CSAX result in the decline of % *R*. This result may be owing to worsened flocculation.

CONCLUSIONS

Based on the results of the above investigation, the following conclusions may be drawn:

1. CSAX copolymers are obtained by grafting copolymerization reaction of corn starch, AM, and sodium xanthate using EPI as crosslinking reagent and CAN as initiator in aqueous solution.

2. The swelling and solubility of CSt are characterized by SV, and the results show that the performances of solid-liquid separation increase with the increase in the quantity of EPI. The optimal value is EPI = 4 mL.
3. The varieties of CAN and AM lead to the different % GP, % GE, η , and M , which connect the performance of products, The optimal conditions of grafting copolymerization of CSA are as follows: CSt = 2 g, [AM] = 0.939 mol/L, and [CAN] = 6.67×10^{-4} mol/L at 45°C for 3 h,
4. The quantity of NaOH and CS₂ determine the amount of =COO⁻ groups of CSAX. The optimal conditions of xanthation of CSAX are as follows: CSA = 2 g, NaOH = 6 g, and CS₂ = 2.4 mL, at 30°C for 3 h.
5. The flocculation is studied using the optimal conditions of CSAX, which can remove both turbidity causing substances and heavy metal ions from aqueous solutions, i.e., % T = 98.4% and % R = 99.2%, respectively.

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