



Synthesis of crosslinked starch-graft-polyacrylamide-co-sodium xanthate and its performances in wastewater treatment

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ABSTRACT

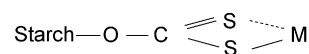
A novel crosslinked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) was synthesized by grafting copolymerization reaction of corn starch, acrylamide (AM), and sodium xanthate using epichlorohydrin (EPI) as cross-linking reagent and ceric ammonium nitrate (CAN) as initiator in aqueous solution. CSAX was characterized by FTIR and element analysis. The performances of CSAX in wastewater treatment were evaluated by flocculation experiment. The results show that the CSAX was successfully synthesized and it has functions of removing both turbidity and copper ions from aqueous solution. It was proved that CSAX is more effective than crosslinked starch xanthate (CSX) and much more effective than crosslinked starch-graft-polyacrylamide (CSA) for removing copper ions. It was also proved that CSAX is little less effective than CSA, but much more effective than CSX for removing turbidity.

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1. Introduction

Flocculation is a process that makes finely divided or dispersed particles aggregate and form large floc so as to be settled and separated from water. The chemicals used in flocculation are known as flocculants. Commercial flocculants are generally categorized into two kinds: inorganic one and organic one. Inorganic flocculants react by charge-neutralization principle, therefore, the dosage of flocculants is large and it produces a lot of sludge. Organic flocculants cause particle destabilization by effectively bridging flocculation. They are divided into natural and synthetic flocculants. Synthetic flocculants are much more effective than natural ones because of their versatile tailorability. But it is reported that graft copolymers of natural polysaccharides, such as cellulose and starch, have some good performances of flocculation and have been used as flocculants [1,2]. Of these graft copolymers, the starch-graft-polyacrylamide is the most important one, which can efficiently aggregate, dispersed particles in aqueous solution [3,4]. Generally, the flocs formed by applying flocculants alone will co-precipitate with heavy metal ions, but this co-precipitation result in very inefficient heavy metal ions removal [5]. Therefore, such an additional process as chemical precipitation, electrodialysis, ion exchange and reverse osmosis techniques must be employed to remove heavy metal ions from industrial effluents, but it will enhance running expense in spite of their effectiveness in metal ion removal. Because

the solubility product (K_{sp}) values of metal sulfides are the lowest in all insoluble metal salts and metal hydroxides, the attempts have been made to removal heavy metal ions through the formation of metal sulfides. Wing et al. have reported that a water-insoluble product crosslinked starch xanthate (CSX) was prepared by the xanthation of a highly crosslinked starch (CSt) and was effective for removing heavy metal ions from water without a cationic polymer [6]. When CSX is applied to wastewater, the chelation is generated between CSX and heavy metal ions, and the produced compounds are insoluble in water, therefore, can be settled and separated from water. The chelate complex was expressed as follows [7]:



But it is necessary that the large dose of CSX be used to remove heavy metal ions, therefore this process produce a lot of sludge [8].

According to status quo, this research tries to use a chemosynthesis method to induce the pendant chain PAM and the strong

ligand -C(=S)-SH group into CSt, so as to produce a new flocculant which cannot only reduce the content of substance causing turbidity in water by its PAM pendant chains, but also remove dissolved

metal ions by its the -C(=S)- groups and the -COO^- groups generated by hydrolysis of -CONH_2 [9].

This new flocculant on the basis of starch-graft-polyacrylamide-co-sodium xanthate (CSAX) is prepared by first cross-linking starch, in which epichlorohydrin (EPI) is used as the cross-linking reagent, and then grafting polyacrylamide chains to crosslinked starch (CSt) by ceric ammonium nitrate (CAN) as an initiator, thus crosslinked

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starch-graft-polyacrylamide (CSA) is obtained, at last xanthating CSA via reacting with carbon disulfide in the presence of NaOH. It is confirmed that the cross-linking reaction makes starch form a network structure. The copolymerization grafts flexible PAM chains onto CSt network backbone, which leads to both rigid and flexible steric structure that may be important for flocculation and precipitation. Through cross-linking → grafting → xanthating reaction, we have gained a new kind of semi-soluble product with different functional groups. It is the first time to make PAM chains grafted into CSt and then xanthated. Thus, the starch is endowed with new function of trapping dissolved heavy metal ions and removing suspended particle in aqueous solution.

2. Experiments

2.1. Materials

Corn starch (Food grade) was supplied by flour mill of 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. Epichlorohydrin (EPI) was used as cross-linking reagent. Kaolin, carbon disulfide, acetone (AR, Tianjing Chemical Reagent Factory, Tianjing, China) and other compounds were used as purchased.

2.2. Preparation of crosslinked starch (CSt)

CSt were prepared in the following procedures [10–12]:

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

2.3. Preparation of crosslinked starch-graft-polyacrylamide (CSA)

A series of the CSA samples were prepared by using different amounts of initiator, CSt and AM in the following procedures: CSt (2 g) was treated with distilled water (20 mL) to prepare uniform slurry, and AM solution (40 mL) was added. The mixture was put in a 250-mL three-necked flask equipped with a stirrer, a thermometer and a gas inlet system for nitrogen supply. The flask was immersed in a water bath and heated to 45 °C under nitrogen atmosphere. The predetermined volume of CAN solution was added as known molar solution in 1 mol/L HNO₃. The polymerization was continued by constantly stirring and maintained at a nitrogen atmosphere for 3 h. After desired reaction period, nitrogen supply was stopped and the graft copolymer cooled to 20 °C (room temperature) [13]. The polymer was precipitated in acetone and then the crude products dried in a vacuum oven at 60 °C.

This crosslinked starch-graft-polyacrylamide (CSA) is not soluble in water, therefore it can be called as insoluble starch-graft-polyacrylamide (ISA) which has not been reported so far.

2.4. Preparation of CSAX

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

in a water bath for 3 h until it turned saffron yellow. The product was cooled to 20 °C (room temperature). It was precipitated and filtered and washed with acetone (50%) three times, pure acetone one time, dried at 25 °C to a constant weight, and its character was confirmed by FTIR and elemental analysis.

2.5. Flocculation test

Four gram per liters of CSAX, 5% suspension of kaolin and 10 g/L CuSO₄ solution were prepared as stock solutions.

Four hundred milliliters of tap water and 1 mL CuSO₄ solution or/and 5 mL kaolin suspension were added to a jar (500 mL). The pH of water sample in the jar was adjusted to desired values. Such six jars were placed on the six-joint-stirrers. The CSAX solutions were added in different dosage of 0, 4, 5, 6, 7, and 8 mL, respectively to each jar which were stirred by stirring blades in the water samples at uniform speed of 140 r/min for 2 min, then a slow stirring at 40 r/min for 10 min. Later, a settling time of 10 min was required. The supernatants were drawn. Then the turbidity removal rates were measured by the turbidity meter (Hanna instruments, Italy) and the heavy metal ions removal rates were measured by 220FS atomic absorption spectrometer (Corporation, Varian, USA), respectively.

2.6. Characterization

The FTIR spectrum of the CSAX was recorded on a NEXUS 670SX (Nicole Instrument Corporation, USA) with KBr dispersion method. The FTIR spectra were in the range of 4000–400 cm⁻¹. Elemental analysis studies of dry samples were performed on a Vario EL elemental analyzer (Elemental Instrument Corporation, Germany). Thus, four elements, i.e., carbon, hydrogen, nitrogen and sulfur were confirmed.

3. Results and discussion

3.1. FTIR spectra and elemental analysis

The infrared spectra of CSAX and CSt are shown in Fig. 1. In Fig. 1(b), the peak observed at 3401 cm⁻¹ is due to the stretching vibration wavenumber of the –OH groups. The bands around 1159 and 2931 cm⁻¹ are assigned to –CO stretching and –CH stretching vibration, respectively. Two strong bands around 1016 and 1081 cm⁻¹ are due to –CH₂–O–CH– stretching vibration. A band at 1422 cm⁻¹ is due to the –CH₂ scissoring vibration. It is further noted that –CH bending of –CH₃ (symmetric) and OH in-plane bending vibrations appear at 1463 and 1368 cm⁻¹, respectively. The bands at 929, 765 and 709 cm⁻¹ are due to the pyranose ring vibrations. The absorption peaks at 575 cm⁻¹ is attributed to –OH group on starch [14].

In Fig. 1(a), a broad absorption band at 3386 cm⁻¹ is for the –NH stretching wavenumber of the –NH₂ group, 1758 and 1735 cm⁻¹ corresponding to the –COO⁻ stretching vibration (–COONa), 1663 cm⁻¹ and 1563 cm⁻¹ corresponding to the –C=O stretching vibration (–CONH₂). As homopolymer of AM is removed from reaction mixture, it is suggested, therefore, that graft copolymerization takes place during the reaction. Absorption peaks appear at 2550 cm⁻¹ corresponding to the –SH stretching vibration of the

xanthate unit. The $\begin{matrix} \text{S} \\ || \\ -\text{C}-\text{SH} \end{matrix}$ groups' spectra are displayed in the range of 1250–1200 cm⁻¹, 1140–1110 cm⁻¹ and 1070–1020 cm⁻¹.

The peak at 888 cm⁻¹ may be attributed to the $\begin{matrix} \text{S} \\ || \\ -\text{C}-\text{SH} \end{matrix}$ deformation. It is suggested, therefore, that CSA has been successfully xanthated [15].

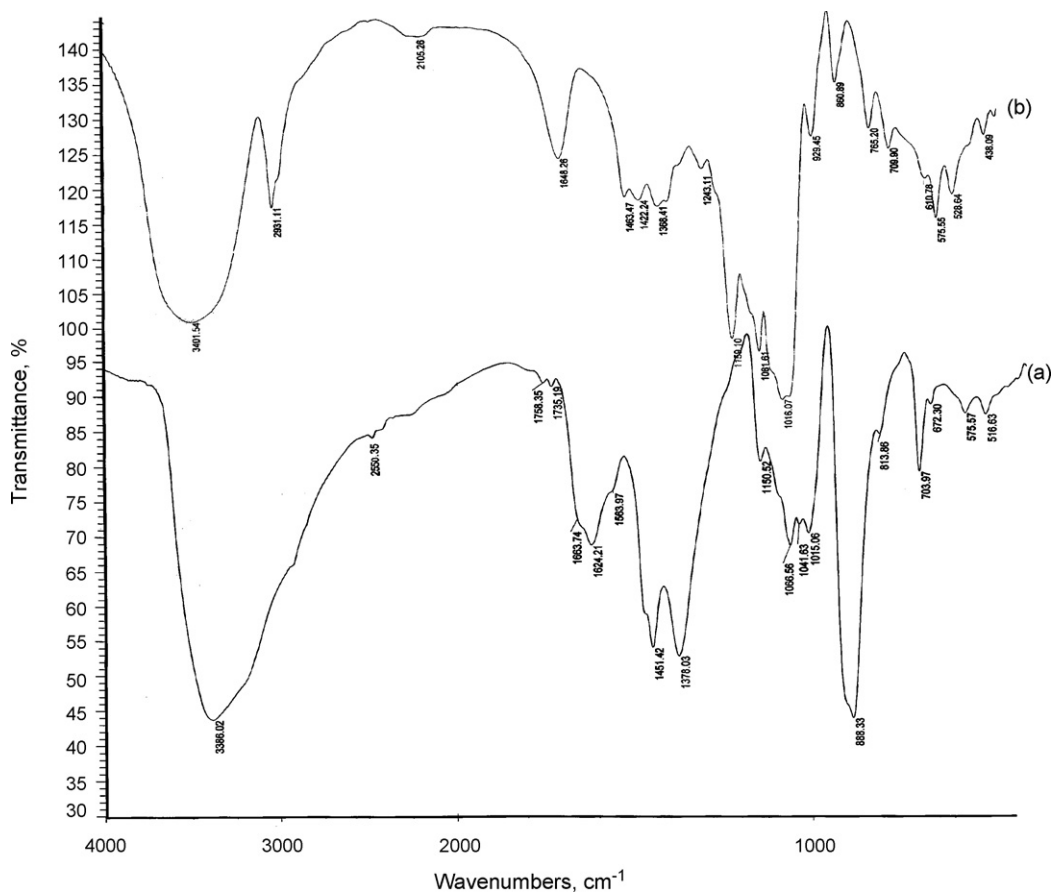


Fig. 1. Infrared spectra of: (a) crosslinked starch-graft-polyacrylamide-co-sodium xanthate and (b) crosslinked starch.

The elemental analysis studies of dry samples shows that CSAX contains 19.03% carbon, 3.84% hydrogen, 2.59% nitrogen and 7.41% sulfur, respectively.

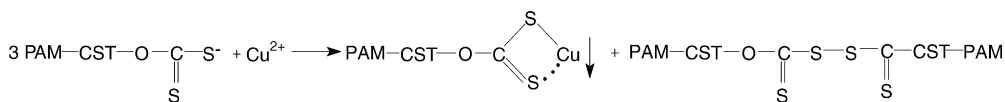
These above analysis results prove that CSAX has been successfully synthesized.

3.2. The performance of CSAX in wastewater treatment

The performance of CSAX in wastewater treatment was evaluated by flocculation experiment. Composite wastewater and experimental procedure are described above in jar test section of this article. The experiment results and discussion is as follows.

3.2.1. Effect of Cu^{2+} ions concentration on its removal

The pH values of water samples that have different concentration of Cu^{2+} ions were adjusted to 5.0. Jar tests were done for these samples. The result is shown in Fig. 2. It shows that the removal Cu^{2+} increases with increasing in the dosage of CSAX, that is, greater dosage of CSAX is required for greater concentration of Cu^{2+} ions. There seems to be a stoichiometry relationship between Cu^{2+} ion and CSAX. It can be explained by following reaction:



It shows that Cu^{2+} ion is reduced to Cu^+ ion by xanthogenate groups on CSAX molecule, and then the chelation compound between CSAX and Cu^+ ion forms.

3.2.2. Comparison of CSAX with CSA and CSX

The performances of CSAX in removing copper ions and turbidity were compared with that of CSA and CSX, respectively. The wastewater samples used in these tests contain 25 mg/L of copper ions or 100 NTU (turbidity unit) of turbidity. Fig. 3 shows that CSAX is more effective than CSX and much more effective than CSA for removing copper ions. It can be explained as follows.

CSAX has not only xanthogenate groups but also the $-\text{COO}^-$ groups generated by hydrolysis of $-\text{CONH}_2$ on its macromolecule pendant chains. Both of them can coordinate copper ions in solutions. But CSX has only xanthogenate groups, and CSA has only $-\text{COO}^-$ groups, therefore they are less effective than CSAX for removing copper ions.

Fig. 4 shows that CSAX is little less effective than CSA and much more effective than CSX for removing turbidity. It can be explained as follows.

CSAX has PAM pendant chains that may be shorter than that in CSA molecule, but CSX has no PAM pendant chains, therefore CSA remove turbidity little more effectively than CSAX and CSX remove turbidity much less effectively than CSAX.

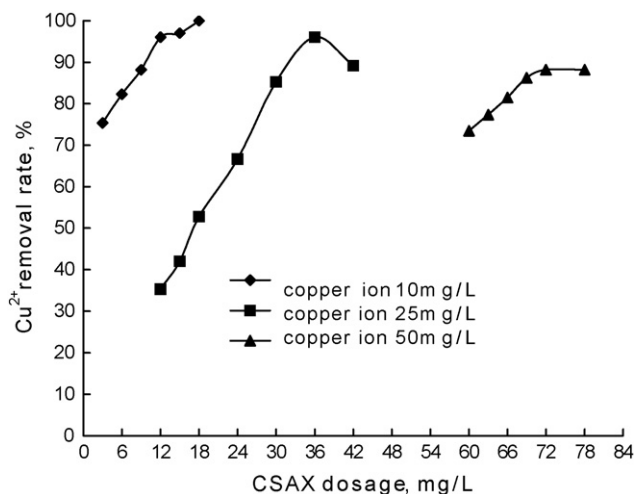


Fig. 2. Effect of concentration of Cu²⁺ on its removal.

3.2.3. Effect of pH on removal of Cu²⁺ ions

The pH values of the wastewater samples containing 25 mg/L copper ions were adjusted to various values from 2.0 to 5.0 by using hydrochloric acid. Jar tests were performed for these samples, and the different dosages of CSAX were added. According to the results shown in Fig. 5, it can be concluded that the removal rate of copper ions increases with the increasing in pH. The effect of pH value on the removal of copper can be explained as follows.

When the pH is raised, more xanthogenic acid groups of macromolecules ionize to negative xanthogenic acid radical groups, so that the chelation between xanthogenic acid radicals and copper ions increases. As a result, the more efficient removal of copper ions can be obtained.

3.2.4. Effect of anions on the removal of Cu²⁺ ions

The pH values of the wastewater samples containing 25 mg/L copper ions were adjusted to 5.0 by using hydrochloric acid, and three kinds of salts, NaCl, Na₂SO₄ and Na₂-EDTA, were added in different concentration, respectively. Jar tests were performed for these samples. In order to enhance the competition of other anions, all the dosages of CSAX were kept to be the same as 20 mg/L which

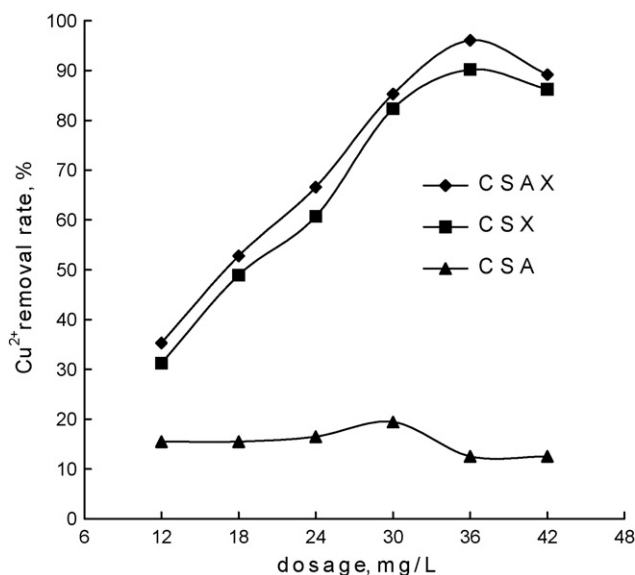


Fig. 3. Comparison of CSAX with CSX and CSA in removing copper ions.

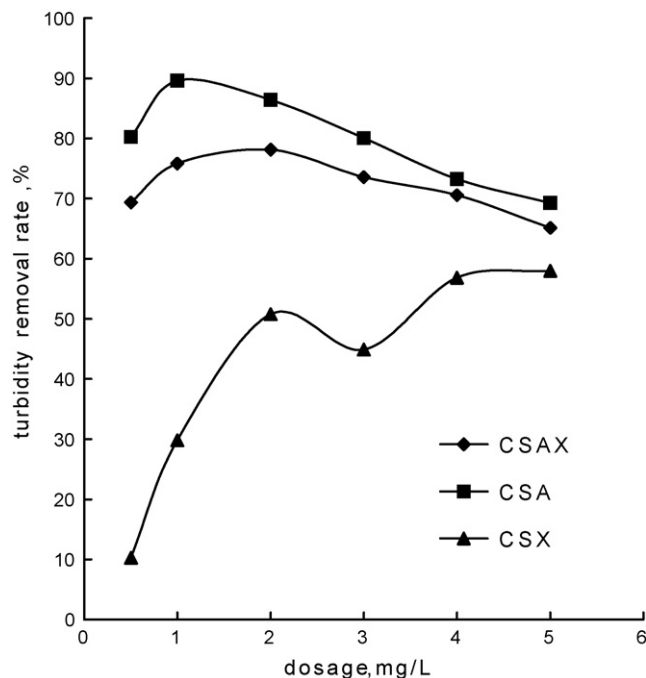


Fig. 4. Comparison of CSAX with CSX and CSA in removing turbidity.

is not enough for the optimum removal. The results are shown in Fig. 6. It can be seen that Cl⁻ ion has no effect on the removal of Cu²⁺ ions; SO₄²⁻ has a little effect on the removal of Cu²⁺ ions, the removal rate decreases slowly with the increasing in the concentration of SO₄²⁻ ion; Among these three anions, EDTA anion has the greatest effect on the removal of Cu²⁺ ions, the removal rate decreases quickly with the increasing in the concentration of EDTA anion. The results can be explained as follows.

There are competitions of anions for coordination with Cu²⁺ ions in the solutions. Because Cl⁻ anion is the weakest coordination group among the three kinds of anions, it decreases the chelation of CSAX with Cu²⁺ ions least, so that the removal rate of Cu²⁺ ions

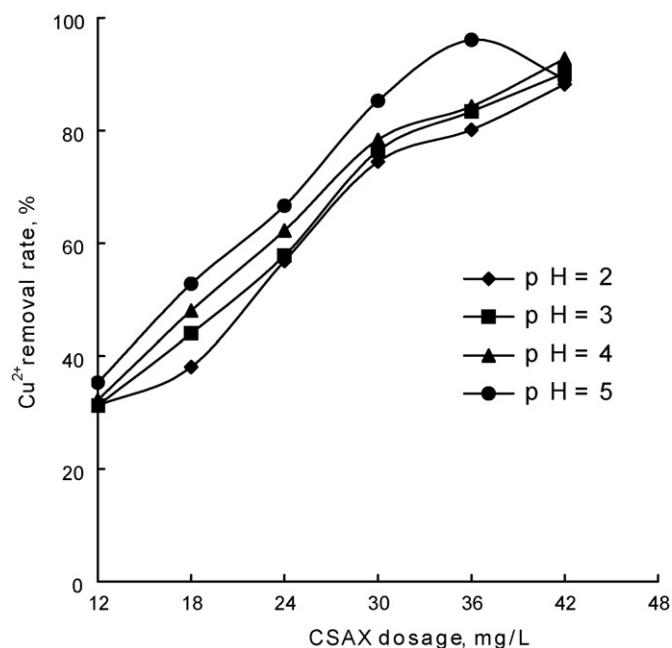


Fig. 5. Effect of pH on removal of copper ions.

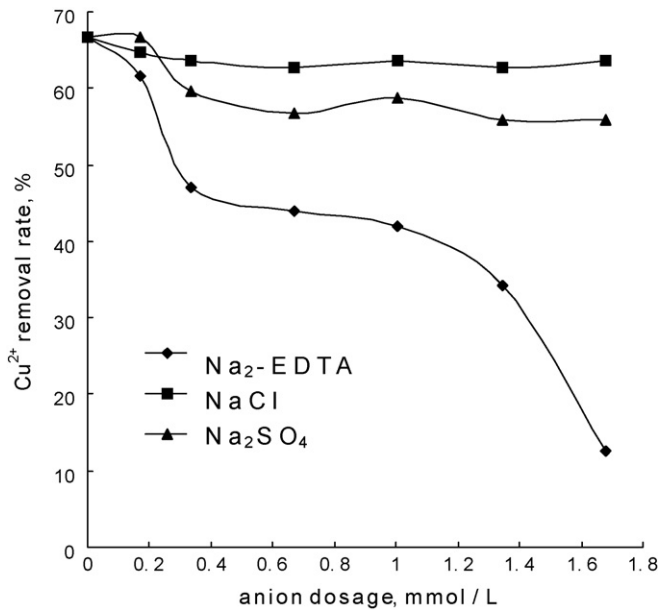


Fig. 6. Effect of anions on the removal of Cu²⁺ ions.

is decreased least. Because EDTA anion is the strongest coordination group among the three kinds of anions, it decreases the chelation of CSAX with Cu²⁺ ions most, so that the removal rate of Cu²⁺ ions is decreased most. This result implies CSAX has higher ability of competition for copper ions than Cl⁻ anion and SO₄²⁻ anion, but lower ability of competition for copper ions than EDTA.

3.2.5. Treatment of water containing both turbidity and copper ions

The samples of wastewater used in these tests contained both turbidity (100 NTU) and copper ions (25 mg/L). The pH values of these wastewater samples were adjusted to 5.0 by using hydrochloric acid, and jar tests were performed for these samples. The result is shown in Fig. 7. In this figure, TRc is defined as the turbidity removal when water sample contains both turbidity (100 NTU) and copper ions (25 mg/L), CR is defined as the copper ions removal when water sample contains only copper ions (25 mg/L). It can be seen from this figure that CSAX can remove heavy metal ions and turbidity at the same time.

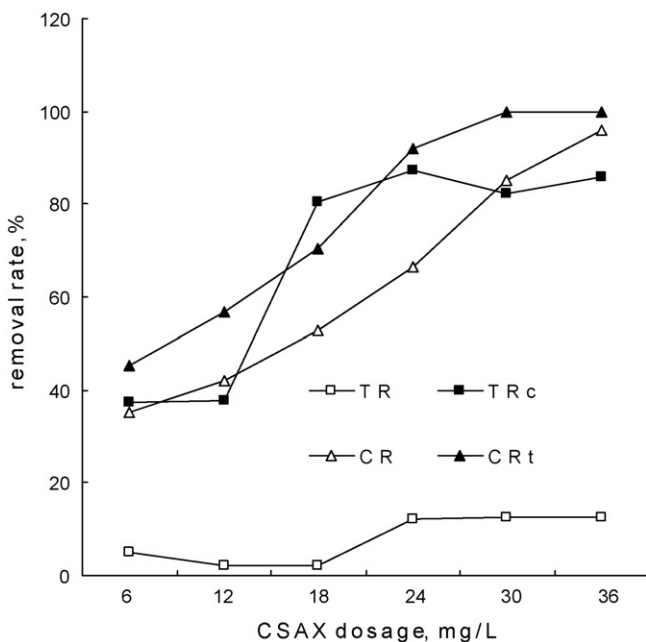


Fig. 7. The treatment of water sample containing both turbidity and copper ions.

copper ions (25 mg/L), TR is defined as the turbidity removal when water sample contains only turbidity (100 NTU); CRt is defined as the copper ions removal when water sample contains both turbidity (100 NTU) and copper ions (25 mg/L), CR is defined as the copper ions removal when water sample contains only copper ions (25 mg/L). It can be seen from this figure that CSAX can remove heavy metal ions and turbidity at the same time.

Comparing TRc with TR and comparing CRt with CR, it can be concluded that the turbidity of wastewater can promote the removal of copper ions and copper ions in wastewater can promote greatly the removal of turbidity. It can be explained as follows.

On the one hand, the floc formed from substances causing turbidity has the "sweep" function for the insoluble colloidal chelate compound of copper with CSAX and the weak adsorption function for soluble copper ions. Therefore, the removal of copper is increased when wastewater samples have turbidity. On the other hand, positive copper ions not only neutralize the negative charges of xanthogenic acid radical groups of CSAX macromolecule because of chelation, but also neutralize the negative charges of the substances causing turbidity, thus reducing the repulsion between the xanthogenic acid radical groups of CSAX and turbidity particles and therefore strengthening the flocculation greatly. It is noted from Fig. 4 that turbidity removals decrease with the increasing in dosage because of excess dosage for the water sample which contains only turbidity. But in this test, the dosages are not excess for water samples which contain both turbidity and copper ions although the dosages are greater than that in Fig. 4. Therefore turbidity removals do not decrease with the increasing in dosage.

4. Conclusions

A synergetically acting new flocculation is synthesized by grafting copolymerization reaction of corn starch, AM, and sodium xanthate using EPI as cross-linking reagent and CAN as initiator in aqueous solution. As a result, two kinds of groups with different functions are induced into CSAX with network structure. So, CSAX not only has the good effect of flocculation but also has the capacity to trap heavy metal ions:

- There seems to be a stoichiometry relationship between Cu²⁺ ions and CSAX;
- CSAX is more effective than CSX and much more effective than CSA for removing copper ions; CSAX is little less effective than CSA and much more effective than CSX for removing turbidity;
- The removal rate of copper ions increases with the increasing in pH of water sample;
- Cl⁻ ion has no effect on the removal of Cu²⁺ ions, but the removal rate decreases slowly with the increasing in the concentration of SO₄²⁻ ion and decreases quickly with the increasing in the concentration of EDTA anion. This result implies CSAX has higher ability of competition for copper ions than Cl⁻ anion and SO₄²⁻ anion, but lower ability of competition for copper ions than EDTA;
- Copper ions and turbidity have a cooperative removal effect with each other in the process of treating wastewater containing both copper ions and turbidity.

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