

## The Characteristic of Macromolecule Heavy Metal Flocculant and Trapping CSAX of $\text{Hg}^{2+}$ from Aqueous Solutions

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**Abstract.** In this paper, the flocculant and trapping performance of the crosslinked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) was evaluated using wastewater that contains  $\text{Hg}^{2+}$  as the target. Some factors affect the removal rate of  $\text{Hg}^{2+}$  were investigated. The experimental results show that the CSAX was successfully synthesized and it has functions of removing both turbidity and  $\text{Hg}^{2+}$  from aqueous solution. With the increase of pH value and CSAX dosage, the removal rate of  $\text{Hg}^{2+}$  is increased gradually. If the presences of alkali metal and alkaline-earth metal ions in wastewater, the removal rate of  $\text{Hg}^{2+}$  is improved too. Then the presences of  $\text{SO}_4^{2-}$  and EDTA in wastewater inhibit the removal rate of  $\text{Hg}^{2+}$ . Meanwhile when  $\text{Hg}^{2+}$  and turbidity coexist in the wastewater, the removal rate of  $\text{Hg}^{2+}$  can be promoted.

### Introduction

At present, a large amount of wastewater containing mercury will produce in nonferrous metal smelting industry, chlor-alkali industry, and electronic industry, etc [1,2]. If it directly discharged into water body, the mercury is a well-known highly toxic metal, considered a priority pollution. Through the physical, chemical and biological functions, the mercury and its compounds will form various forms of mercury, even into very poisonous methyl compounds, which seriously pollute the water environment [3].

Flocculation precipitation is an important method of water treatment [4]. It 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 organic polymer flocculant has been widely employed in water and wastewater treatment because of its large specific surface area and particle destabilization by effectively bridging flocculation. Generally, the flocs formed by applying flocculants alone will co-precipitate with heavy metal ions, as well as contained chelating agent in heavy metal wastewater, heavy metal ions are easy to be stabilized too, so this co-precipitate result in very inefficient heavy metal ions removal. Because it is difficult competition between the conventional polymer flocculation ligands and the complexes ligands, the varieties of existing flocculant do not effectively remove dissolved metals [4,5].

A novel crosslinked starch-graft-polyacrylamide-co-sodium xanthate (CSAX) was synthesized by grafting copolymerization reaction of corn starch, acrylamide (AM), and sodium xanthate. The

CSAX has been introduced strong ligands of heavy metal ions, such as  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$  and  $-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}^-$ , which result in the flocculant with the function of heavy metal captured. The CSAX depends on its chelation can convert dissolved heavy metal ions into insoluble sediments. In addition to the CSAX has the length of PAM pendant chains that remove turbidity by bridging flocculation. So it is possible that the CSAX use as flocculant to reduce the subsequent units in wastewater treatment [6,7].

## Experimental Sections

### Materials

Corn starch (food grade) was supplied by local packing house, Lanzhou, China. Acrylamide (AM) was provided by Shanghai Chemical Reagent Factory, Shanghai, China, and ceric ammonium nitrate by Beijing Chemical Reagent Corp., Beijing, China. Kaolin, mercuric chloride, epichlorohydrin, acetone (Tientsin Chemical Reagent Factory, Tientsin, China) and other substances were used as purchased.

### Preparation of Crosslinked Starch (CSt) [6,7]

Corn starch (50g) and 1% (w/v) sodium chloride solution (75mL) were put in a 250mL 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. KOH solution (15%, w/v; 20 mL) was added to this slurry, and then EPI added dropwise for about 5min. After 8 h, the reaction was completed. CSt suspension slurry was adjusted to pH 7.0 with 1M HCl and 1 M NaOH solution, as well as filtered through a coarse fritted-glass funnel and the solid was washed successively with distilled water, and several portions of ethanol. After dried in a vacuum oven at 60 °C to a constant weight, the CSt was milled and screened.

### Preparation of Crosslinked Starch-Graft-Polyacrylamide (CSA) [6,7]

A series of the CSA samples were prepared by using different amounts of initiator, CSt and AM in the following procedures: CSt (2g) was treated with distilled water (20mL) to prepare uniform slurry, and AM solution (40mL) 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 1M HNO<sub>3</sub>. The polymerization was continued by constantly stirring and maintained at a nitrogen atmosphere for 3h. After desired reaction period, nitrogen supply was stopped and the graft copolymer cooled to room temperature. The polymer was precipitated in acetone and then the crude products dried in a vacuum oven at 60 °C.

### Preparation of CSAX [6,7]

CSA (1g) was xanthated by adding 3M NaOH and CS<sub>2</sub> into the sealed conical flask and stirring magnetically at 30°C in a water bath for 3h until it turned saffron yellow. The products were cooled to room temperature. It was precipitated and filtered and washed with acetone (50%) three times, pure acetone one time, dried at 30°C to a constant weight.

### Flocculation Test

1g/L CSAX, 1% (w/v) kaolin suspension and stock solutions containing Hg<sup>2+</sup> (25g/L) were prepared using mercuric chloride. 400 mL of distilled water and 1 mL mixed metal ions in solution were added a series of 500 mL beakers. The pH of the solutions was adjusted with 1M HCl solution and 1M NaOH, which was monitored by 828 pH/ISE acidometer. The beakers were placed on TS6 program-controlled mixing coagulation experiment instrument. The CSAX solution was added in different dosage to different beakers, which were stirred at uniform speed of 140 rpm for 2 min, then at 40 rpm for 10 min. When quickly stirred, the flocculant can be mixed completely. As slowly stirred, the formed floc has enough time to grow up, as well as it can be settled fully. Then the precipitates were allowed to settle for 10 min and the supernatant removed. The Q (removal rate of Hg<sup>2+</sup>) was measured by SG921 mercury measurement instrument, and calculated as follows:

$$Q = 100 (Q_0 - Q_1) / Q_0$$

Where Q<sub>0</sub>, and Q<sub>1</sub> are the Hg<sup>2+</sup> concentrations of the initial suspension and supernatant, respectively.

## Results and Discussion

### Effect of pH on Removal Rate of $Hg^{2+}$

Usually the industrial wastewater has a low pH value and high concentrations of heavy metal ions. So the pH value of wastewater samples was adjusted between 2.0 and 5.0 using 1M HCl solution. When the flocculation tests was carried out at the sample water containing the concentration of  $Hg^{2+}$  (25 mg/L), adjust the water samples of different pH value. The CSAX solution was added in different dosage to different beakers. After flocculating settling Q was calculated through the residual concentration of  $Hg^{2+}$ . The effect of pH on Q is shown in figure 1.

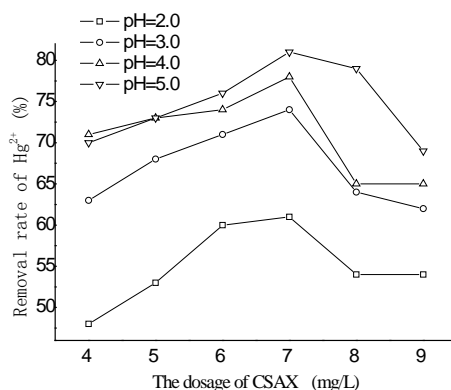


Fig. 1. Effect of pH on removal rate of  $Hg^{2+}$

From figure 1, the pH has great effect on Q. When the pH is raised, Q increases with the increasing in pH value. The  $Q_{max}$  is observed at pH 5.0. The increased Q 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  $Hg^{2+}$  increases. As a result, the more efficient removal of  $Hg^{2+}$  can be obtained.

### Effect of $Na^+$ , $Mg^{2+}$ and $Ca^{2+}$ on Removal Rate of $Hg^{2+}$

When the flocculation tests were carried out at the sample water containing the same pH (5.0), [ $Hg^{2+}$ ] (25 mg/L) and water samples of turbidity (100NTU). we added the different dosage of CSAX and 2mmol/L NaCl, 1mmol/L  $MgCl_2$ , 1mmol/L  $CaCl_2$  into the water samples, respectively. After flocculating settling Q was calculated through the residual [ $Hg^{2+}$ ]. In the meantime, the same experiment was carried out three times. The results as shown in figure 2.

It can be seen from figure 2 that the sample water containing  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  promotes Q. Because  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  belong to the alkali metal or alkaline earth metal, according to the theory of hard and soft acid-base, soft alkali of CSAX cannot coordination with  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  or the coordination ability is poor [8]. They are no effect chelate reaction between CSAX and  $Hg^{2+}$ . However, the presence of  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  will compress electric double layer, because of charge neutralization, reduce the zeta potential, and accelerate the flocculation, so as to increase Q. The promotion of  $Na^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  follow  $Mg^{2+} > Ca^{2+} > Na^+$ .

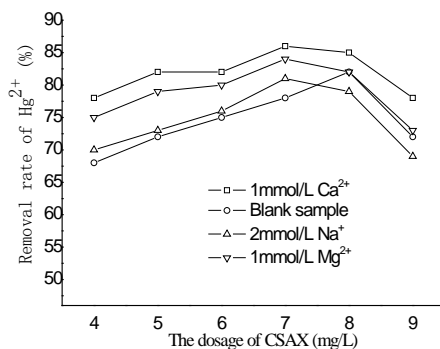


Fig. 2. Effect of Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> on removal rate of Hg<sup>2+</sup>

### Effect of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and EDTA on Removal Rate of Hg<sup>2+</sup>

When the flocculation tests were carried out at the sample water containing the same pH (5.0), [Hg<sup>2+</sup>] (25 mg/L) and water samples of turbidity (100NTU). we added the different dosage of CSAX and 0.05mmol/L Na<sub>2</sub>-EDTA, 0.05mmol/L Na<sub>2</sub>SO<sub>4</sub> and 0.1mmol/L NaNO<sub>3</sub> into the water samples, respectively. After flocculating settling Q was calculated through the residual [Hg<sup>2+</sup>]. The same experiment was carried out three times. The results as shown in figure 3.

It can be seen from figure 3 that NO<sub>3</sub><sup>-</sup> has no effect on Q. SO<sub>4</sub><sup>2-</sup> has a little effect on Q, the Q decreases slowly with the increasing in [SO<sub>4</sub><sup>2-</sup>]. But EDTA has the greatest effect on Q among these three anions. The results can be explained as follows.

There are competitions of anions for coordination with Hg<sup>2+</sup> in the solutions. Because NO<sub>3</sub><sup>-</sup> is the weakest coordination group among these three anions, it least decreases the chelation of CSAX with Hg<sup>2+</sup>, so that Q is decreased least. However EDTA is the strongest coordination group among them, it most decreases the chelation of CSAX with Hg<sup>2+</sup>, so that Q is decreased most. This result implies CSAX has higher ability of competition for Hg<sup>2+</sup> than SO<sub>4</sub><sup>2-</sup>, but lower ability of competition for Hg<sup>2+</sup> than EDTA.

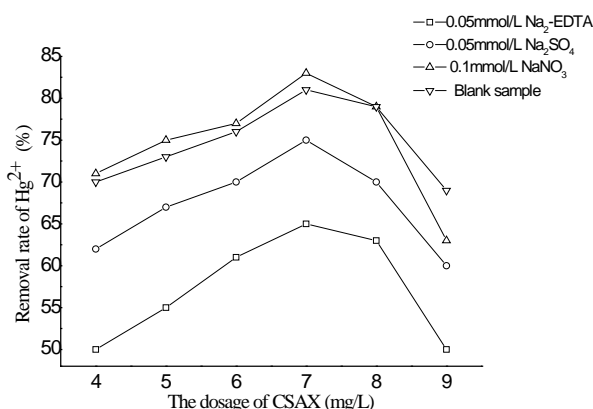


Fig. 3. Effect of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and EDTA on removal rate of Hg<sup>2+</sup>

### Effect of Turbidity on the Removal Rate of Hg<sup>2+</sup>

When the flocculation tests were carried out at the sample water containing the same pH (5.0) and [Hg<sup>2+</sup>] (25 mg / L) adjust the water samples of different turbidity (65 NTU, 200 NTU), thus the different dosage of CSAX was added. After flocculating settling Q was calculated through the residual [Hg<sup>2+</sup>]. The results as shown in figure 4.

It can be seen from figure 4 that the turbidity promotes Q. Under the same CSAX additive dosage, the promoting effect increased with the increase of turbidity. Due to the increase of turbidity, the same distance CSAX molecules can capture a lot of the mucus particles. The greater the volume of flocs grows, the more specific surface area of the flocs generate. The ability of Hg<sup>2+</sup> of adsorption,

synergy and swept volume increase, so that the removal rate of  $\text{Hg}^{2+}$  improves. In addition,  $\text{Hg}^{2+}$  and the mucus particles interact to take off and have a higher chance of coagulation sink in the high turbidity.

CSAX can be used to remove both the turbidity and  $\text{Hg}^{2+}$  in the wastewater. The turbidity removal is caused by the long chain molecules, moreover the removal of  $\text{Hg}^{2+}$  has been formed CSAX-Hg chelate through chelating reaction, redox reaction, coordination and ion exchange reaction on CSAX

molecules of  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$ ,  $-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}^-$ . In addition, through the bridging mechanism CSAX and suspended muddy thing can generate large flocs, which have large specific surface area; it can absorb a part of the solubility of  $\text{Hg}^{2+}$  on this surface along with the precipitation of flocs removed [9].

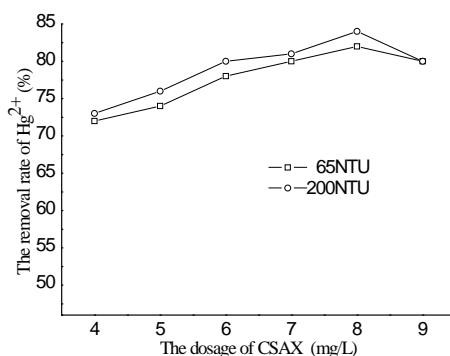


Fig. 4. Effect of turbidity on the removal rate of  $\text{Hg}^{2+}$

## Conclusions

Through analysis and evaluation the performance of CSAX, we have been drawn conclusion as follows:

(1) CSAX belongs to a novel multifunctional flocculant. It can both remove heavy metal ions and turbidity synchronously from acid solutions with  $-\overset{\text{S}}{\parallel}{\text{C}}-\text{SH}$ ,  $-\text{COOH}$  and  $-\text{CONH}_2$  groups.

(2) Under laboratory conditions for pH 5.0, the dosage of the CSAX is 70 mg/L, the initial turbidity is 100 NTU and  $[\text{Hg}^{2+}]$  25 mg/L, The removal rate of  $\text{Hg}^{2+}$  reached 84%.

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