Floc Morphological analysis of macromolecule heavy metal flocculant CSAX

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Abstract. The purpose of the flocculation operation is not only to remove the substance causing turbidity, but also to give the causing particles with the ability to be trapped in subsequent operations. This paper discusses the process of generating the floc, sedimentation characteristics, separation effect and so on, when the macromolecule heavy metal flocculant CSAX used in water treatment, especially for heavy metal ions and turbidity of coexisting system. The research is the popularization and application of this kind of flocculant that expand the types of multifunctional flocculant, decreases the number of the water treatment unit, which provides a certain reference value.

1. Introduction

Heavy metal wastewater is produced in many production processes of mining, metallurgy, machinery manufacturing, chemical industry, electronics, instrument and other industries. For example, in the process of metal surface processing, especially in the process of electroplating, the rinsing wastewater and bath waste liquid containing chromium, cadmium, copper, zinc, nickel and other heavy metals and cyanide are discharged. Because these heavy metals cannot be degraded by microorganisms, they become persistent pollutants, which greatly harm the ecological environment and people's health.

The heavy metal ions discharged into the water environment are usually in complexation or coordination state, and the commonly used methods can not decompose the damaged ones, but can only transfer their existing location and transform their physical and chemical forms. For these dissolved heavy metals, the common treatment methods are adding chemical precipitation treatment before the flocculation treatment unit, or adding ion exchange, adsorption, and reverse osmosis after the flocculation unit. Dialysis, electrodialysis and other treatment units for further depth treatment, which increase the number of treatment units, Those operations are bound to greatly raise the cost of treatment.

In recent years, Professor Qing Chang's team found that some of the strong coordination group of heavy metal ions by reaction is connected to the polymeric flocculant can give its capture function of heavy metal ions[1], this kind of macromolecule flocculant used in water treatment of heavy metals of flocculation unit, polymeric flocculant can not only through the matrix of "electrical neutralization", "bridging flocculation" and "the trap swept volume" action such as to reduce the amount of turbid substance in water, also can rely on coordination or chelation remove dissolved heavy metals in water, thus can reduce the number of subsequent processing unit, reduce the processing cost.

The main mechanism of macromolecule heavy metal flocculant CSAX for trapping heavy metal ions includes heavy metal ions and their molecules of disulfide generation of carboxyl ligand or chelation, at the same time it also involves the coordination of amine or hydroxyl groups (generated by...
hydrolysis) on the side chain of PAM, especially disulfide generation of carboxyl chelation play main capture function[2], it can be the chelation between heavy metal ions and more than two adjacent coordination groups on the same molecular chain, or the chelation between heavy metal ions and coordination groups that belong to multiple molecular chains, taking the latter as an example, which is expressed as follows:

\[ \text{PAM} \rightarrow \text{CS} \rightarrow \text{O} \rightarrow \text{C} \rightarrow \text{S} \rightarrow \text{M} \rightarrow \text{S} \rightarrow \text{C} \rightarrow \text{O} \rightarrow \text{CS} \rightarrow \text{PAM} \]

2. Materials and Methods
Take six 500mL beakers and fill them with 400mL running water, add 1mL of heavy metal salt reserve solution respectively, the prepared water sample contains 25mg/L metal ions, and 5mL kaolin suspension is added which make the turbidity of the prepared water sample 100NTU, then the beakers were placed on a six-way agitator, and 30 mg/L of CSAX solution was added, respectively. The pH values were adjusted to 2.0, 3.0, 4.0 and 5.0 with 1mol/LHCl and 1mol/LNaOH solutions, at the same time, a uniform stirring speed of 140r/min was used for 2 minutes, then it was stirred at a slow speed of 40r/min for 10 min, and settled for 10 min at last. A small amount of the floc deposited on the bottom of the beaker was placed on the slide with a sampling spoon, observed and photographed under a microscope, and the image was processed[3].

3. Results & Discussion
3.1. Flocs formed by CSAX and cationic metal ions (Take Cu\(^{2+}\) as an example)

(a) pH=2.0
(b) pH=3.0
From figure 1 analysis, when pH=2.0, the flocs formed are larger, with higher voidage, less dense settlement and higher water content. The main reason is CSAX molecules stretch, and molecules of the CSAX xanthate has the strong reducibility that Cu^{2+} is reduced to Cu^{+}, and generate CSAX - Cu(I) chelate flocs at a lower pH[4]. In addition at pH = 2.0, The surface of suspended kaolin particles is positively charged. Electrostatic neutralization occurs with negatively charged CSAX molecules, which produce obligate adsorption. Effective bridging flocculation is formed. When pH=3.0 or 4.0, the floc structure is dense, the degree of irregularity is reduced, the surface is smooth, the floc particles are small, the voidage is less, the settlement performance is good, and easy to separate. When pH=5.0, The formation of porous flocs has a compact structure, rough surface, with branches and space, and a significant network structure. These indicate that the flocs are more irregular and have more voidages. Adhesion, bridging and net traps are more likely to occur. The synergism and sweep with the suspended turbidity particles of kaolin were obvious.

3.2. Flocs formed by CSAX and metal ions of anion form (Cr (VI), for example)
Analyzed from figure 2, The Cr (VI) usually exist in anionic \( \text{Cr}_2\text{O}_7^{2-} \) form under highly acidic conditions in water. When pH = 2.0, the oxidation of Cr (VI) is stronger, but the xanthic acid group on the CSAX chain has strong reducibility, which reduces Cr(VI) to Cr(III), then CSAX can chelate and precipitate with Cr(III)\[5\]. In the flocculation process, the flocs are in sheet shape and gradually extend and expand. The large flocs are aggregated from the small flocs. The bond between the flocs is strong. This indicates that the adsorption bridging effect between Csax-Cr chelated flocs is dominant. Raise the pH to 5.0, if Cr\(^{3+}\) does not precipitate Cr(OH)\(_3\), The higher the pH value, the higher the ionization degree of the xanthic acid group on the CSAX molecule. Xanthan acid and Cr\(^{3+}\) coordination precipitation reaction occurred, so as to achieve the purpose of the removal of Cr (VI).

4. Conclusions
When the dosage of CSAX is appropriate, there are strong coordination groups of heavy metal ions in the structure of xanthic acid group and the function of flocculation on polyacrylamide side chain, thus can simultaneously trap heavy metal ions and remove turbidity at the same time. It has a strong specific surface area and three-dimensional network structure. On the one hand, metal ions are destabilized by redox reaction, on the other hand, the skeleton of the cross-linked mesh floc changes the situation that the floc is made of a single material as the core. It promotes the flocs with small particle size to grow rapidly and form large flocs with good density and aggregation, which is convenient for the subsequent treatment unit to separate the flocs.

The pH value of water has an important effect on the removal of heavy metal ions and turbidity by CSAX. For Cu\(^{2+}\), With the increase of pH value, the degree of ionization of CSAX molecule increases. The number of xanthic acid groups goes up. On the one hand, Cu\(^{3+}\) can coordinate or chelate with xanthic acid group that generate insoluble in water CSAX-Cu (II) complex. Xanthic acid groups, on the other hand, reduce Cu\(^{2+}\) to Cu\(^+\), which can generate more stable CSAX-Cu (I) chelate with Cu\(^+\). At the same time, the carboxyl functional groups on the CSAX molecular chain also have ion exchange reactions with Cu\(^{2+}\) and Cu\(^+\). These reactions amplify the topological effect of CSAX network structure. So the new flocs are constantly filling into the interior. It gradually forms dense large flocs with good settlement. In the later stage of flocculation, a large number of massive flocs were formed in the water and the water transmittance was good. For Cr (VI), Cr (VI) usually in anionic form exists in the water. It cannot coordinate with the xanthate group of CSAX molecule, but the xanthate group on CSAX molecule has strong reductive property. Reduction of Cr (VI) of Cr\(^{3+}\) under acid condition, the xanthic acid group on CSAX molecule chelates with Cr\(^{3+}\) and precipitates rapidly. Therefore, reducing the pH value is helpful to form a topology network structure.
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