Removal of multiple heavy metal ions using a macromolecule chelating flocculant xanthated chitosan

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ABSTRACT

In this paper, the removal performance and mechanism of xanthated chitosan (XCTS) towards heavy metal ions are investigated. XCTS possesses both strong chelating abilities and excellent flocculation properties, which can effectively remove several kinds of heavy metal ions, such as Cr$^{3+}$, Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$. It has a good potential for practical application. In a flocculation test of a mixed component solution, the removal rates of Cr$^{3+}$, Cu$^{2+}$ and Cd$^{2+}$ reach 100%, 100% and 99.1%, respectively. The removal rates are significantly greater than that of a single component solution. It indicates that there is a synergistic effect between different metal ions. Moreover, the selectivity of XCTS for Cr$^{3+}$ and Cu$^{2+}$ is obviously superior to that for Cd$^{2+}$; XCTS is easier to combine with the heavy metal ions belonging to hard acids.

Key words | chelation precipitation, chitosan, heavy metal wastewater, macromolecule flocculant, removal mechanism, xanthation

INTRODUCTION

The global demand for most heavy metals continues to increase as a result of the rapid development of modern industrial activities, such as metal plating, mining, metallurgy, alloy, machine manufacturing, chemical industry, electronics and instruments. The wastewater has high amount of heavy metals. Heavy metals are persistent pollutants known for their nonbiodegradable properties and bioaccumulation even at trace levels. Accordingly, any kind of heavy metal pollution would increase health risks to humans and other living systems. For that reason, it is crucial to remove the heavy metal contaminants prior to the release of wastewater from the industrial process.

At present, adsorption, ion-exchange and membrane separation are popular and effective methods for the treatment of heavy metal wastewater (Chen et al. 2018; Kaur & Jindal 2018; Li et al. 2018). However, if these methods are going to be applied widely, certain water treatment units need to be added; accordingly the treatment agent regeneration and membrane replacements will increase in cost. Therefore, flocculation using simple equipment is still the most popular method for the treatment of heavy metal wastewater (Chang & Wang 2007; Zhang et al. 2016). In recent years, many studies have shown that the application of polymeric flocculants with strong chelating ability can significantly reduce residual content of heavy metal ions in wastewater compared to traditional inorganic coagulants (Seo et al. 2002; Chang et al. 2008; Zeng & Liu 2013).

Chitosan is a natural organic macromolecule flocculant, and it has been used in widespread research and exerted a tremendous fascination in industrial applications as a flocculation agent for wastewater treatment. Because the molecular chain of chitosan contains a number of –OH and –NH$_2$ groups, which have a certain chelating ability for heavy metal ions, chitosan can be used as a heavy metal trapping agent. However, using chitosan alone as a flocculation agent to treat heavy metal wastewater could not achieve an ideal effect. One reason is the limited solubility of chitosan in an aqueous solution, which limits the number of chelating groups that metal ions can contact (Ahmed & Ikram 2018). Another is that the heavy metal ions cannot be separated from water only by chelating with –OH and –NH$_2$ (Chang et al. 2009). In recent years, researchers have developed many different ways to chemically modify chitosan, which substantially improved the application field and efficiency of chitosan. They grafted some ligands with high metal affinities capable of precipitating metal ions onto the molecular chain of chitosan through chemical synthesis to make it into a water-soluble flocculant.

or some kind of adsorption material, such as by introducing a mercapto-group or carboxylic group into chitosan (Bratskaya et al. 2009; Chang et al. 2009; Chanhan et al. 2012).

In our previous study, xanthated chitosan (XCTS) was successfully synthesized by grafting a xanthogenate group (–OCSS−) onto the molecular chain of chitosan. By this approach, not only the solubility of chitosan was improved over a wide pH range, but its chelating ability with heavy metal ions was enhanced. The –OCSS− group possesses a strong affinity for heavy metal ions, and the solubility product value (Ksp) of heavy metal xanthogenate is usually very small; therefore, XCTS can form an insoluble chelate compound with most species of heavy metal ions in wastewater (Homagai et al. 2010; Liang et al. 2010; Yang et al. 2018). XCTS perfectly combines the capabilities of chelate precipitation and flocculation, which can not only remove turbidity from water by electrical neutralization, bridge and net capture effect but also remove soluble heavy metal ions from water by chelating precipitation, flocculation and adsorption.

XCTS has been successfully applied to the treatment of wastewater containing Cu2+ (Yang et al. 2018). However, the properties of XCTS for the removal of other heavy metal ions have not been systematically investigated. Here, we continue to examine the performance of XCTS on the removal of Cr3+ and Cd2+ from aqueous solution. Moreover, the mechanism of chelation–flocculation is explored, the selectivity of XCTS for heavy metal ions is studied and the possibility of effective removal of other metal ions by XCTS is hypothesized.

## EXPERIMENTAL

### Materials

Chitosan (AR, deacetylation degree 95%, molecular weight 2×10^5 to 4×10^5 Da, particle size 80 mesh, derived from crab shells) was purchased from Shanghai Macklin Biochemical Co. Ltd, Shanghai, China. Benzaldehyde (AR) was provided by Tianjin Kaixin Chemical Industry Co. Ltd, Tianjin, China. CS2 (AR) was obtained from Guangfu Chemical Research Institute, Tianjin, China. HCl (GR) was received from Baiyin Chemical Reagent Plant, Baiyin, China. Cr(NO3)3·9H2O (AR) was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd, Tianjin, China. NaOH (AR), CdCl2·2½H2O (AR) and other reagents (AR) were purchased from Tianjin Damao Chemical Reagent Plant, Tianjin, China.

### Synthesis of XCTS

XCTS was synthesized and used as a sodium salt aqueous solution (Yang et al. 2018). The specific methods for the synthesis of XCTS are as follows. First, 1.0 g of CTS was dissolved in 30 mL of acetic acid (3% solution) and constantly stirred at room temperature for 0.5 h by using a JB-2 thermostatic magnetic stirrer (Shanghai Ray Magnetic Xinjing Instrument Co. Ltd, China). The solution was then diluted with 20 mL of anhydrous ethanol and was placed in a KH5200DB digital ultrasonic cleaner (Kunshan Hechuang Ultrasonic Instrument Co. Ltd, China). A certain amount of benzaldehyde (C6H5CHO:CTS molar ratio was 7:1) dissolved in 20 mL of anhydrous ethanol was added dropwise into the solution after adjusting the solution pH to 6.0 using HCl solution (1 mol·L⁻¹). This mixture was heated to 70 °C in a water bath and underwent constant ultrasonic oscillation for 4 h. A white solid was obtained, which was rinsed with anhydrous ethanol to remove excess benzaldehyde. This was the intermediate product, Schiff-base chitosan. Next, a solution was prepared with 2 mL of CS2 and 50 mL of NaOH (5% solution) at 30 °C and stirred for 30 min. The Schiff-base chitosan was added to the solution. The reaction proceeded for 4 h at 60 °C, yielding a yellowish solution that was used directly in subsequent flocculation tests.

### Flocculation test

Flocculation experiments were performed in a TS-6 jar test instrument (Wuhan Hengling Science & Technology Co., China). Four hundred milliliters of tap water and a certain amount of stock solution of different metal ions (10,000 mg·L⁻¹) were added to a 500 mL jar. The pH value was adjusted to the desired value by using HCl solution (1 mol·L⁻¹). After the addition of different dosages of flocculant (XCTS) solution into the jars, the water samples were stirred rapidly at 120 rpm for 2 min, stirred slowly at 40 rpm for 10 min and allowed to settle for 10 min. The residual metal concentration of supernatant solution was determined by an AA 220FS atomic absorption spectrophotometer (Varian Co., USA). The flocs were filtered, washed sufficiently with distilled water, and then dried to constant weight under vacuum at 55 °C. Afterwards, the structure of the flocs was characterized by Fourier transform infrared (FTIR) spectroscopy, and the micrographs of flocs were filmed by a JSM-5600LV scanning electron microscope (JEOL Co., Japan).
RESULTS AND DISCUSSION

Chelation and flocculation performance

Effect of pH value on the removal rate of Cr\(^{3+}\) and Cd\(^{2+}\)

The pH value is an important parameter which affects the removal of heavy metal ions from the solution. Since hydroxide colloids or precipitates are easily produced in the solution containing metal ions when the pH is greater than 7.0, the pH values of water samples containing 25 mg·L\(^{-1}\) of Cr\(^{3+}\) or Cd\(^{2+}\) were adjusted to 2.0, 3.0, 4.0, 5.0 and 6.0 in this work. The flocculation tests were performed on these water samples at different dosages of XCTS. Figure 1 shows the removal rates of Cr\(^{3+}\) and Cd\(^{2+}\) from single component solutions.

As observed in Figure 1, the removal rate of Cr\(^{3+}\) and Cd\(^{2+}\) was closely related to the pH of the solution. Figure 1(a) shows that the removal rate of Cr\(^{3+}\) increased notably with increasing XCTS dosage at the same initial pH. The maximum removal rate of Cr\(^{3+}\) was 19.6% at pH 2.0, 94.7% at pH 3.0, 98.8% at pH 4.0, 97.5% at pH 5.0 and 92.3% at pH 6.0; the corresponding residual concentrations of Cr\(^{3+}\) were 4.02, 0.26, 0.06, 0.12 and 0.38 mg·L\(^{-1}\). At pH 3.0–6.0, these values were far lower than the 1.5 mg·L\(^{-1}\) limit for the total Cr set by the National Integrated Wastewater Discharge Standard of China. The maximum removal rate of Cr\(^{3+}\) at different pH values tended to increase first and then decrease later with the increase in pH value. At pH 4.0, the maximum removal rate of Cr\(^{3+}\) was the highest value of the corresponding maximum removal rates at all pHs tested. This indicated that pH 4.0 could be chosen as the optimum pH for removing Cr\(^{3+}\) by XCTS. Figure 1(b) shows that the maximum removal rate of Cd\(^{2+}\) was obtained at pH 6.0: the corresponding value was 65.1%. In addition, the removal rate of Cd\(^{2+}\) increased notably with the increase in pH from 2.0 to 6.0. This tendency was in good agreement with the dependence of XCTS electrophoretic mobility on pH. The isoelectric point (pH\(_{IEP}\)) of XCTS, which was measured through a zeta potential method, was pH 2.6 (Yang et al. 2018). When the pH became lower than the pH\(_{IEP}\), the net negative charge of XCTS molecular determined by ionization of the xanthogenate groups decreased due to the protonation of \(-\text{N=}\) in the polymer (Chang & Wang 2007; Wang & Chang 2007; Bratskaya et al. 2009; Liu et al. 2013). Thus, the molecular chain of XCTS accumulated a large amount of positive charge. The probability of a collision between XCTS and positively charged metal ions reduced because of the electrostatic repulsive force. Conversely, when the pH was greater than the pH\(_{IEP}\), the net negative charge of XCTS molecular determined by ionization of the xanthogenate groups increased. As a result of the attraction between positive and negative charges, the chelation collaberation of XCTS and metal ions was enhanced and the efficiency of metal removal increased. Therefore, the removal rate of Cd\(^{2+}\) increased with increasing pH. However, unlike Cd\(^{2+}\), Cr\(^{3+}\) formed chromium hydroxide colloids at lower pH (during the experiment, the obvious turbidity caused by the precipitation of chromium hydroxide was observed at pH 5.0 and 6.0). The combination of OH\(^{-}\) and Cr\(^{3+}\) weakened the chelation of XCTS and Cr\(^{3+}\); so that the sedimentation of flocs, netting and sweeping action of XCTS would also be reduced. Consequently, the removal effect of Cr\(^{3+}\) by XCTS was the best at pH 4.0.

Effect of XCTS dosage on the removal rate of Cr\(^{3+}\) and Cd\(^{2+}\)

Figure 2 shows the effect of XCTS dosage on the removal rate of Cr\(^{3+}\) and Cd\(^{2+}\). Simulated water samples of Cr\(^{3+}\),
and Cd\textsuperscript{2+} were tested at concentrations of 5, 15, 25 and 50 mg·L\textsuperscript{-1} with an initial pH of 4.0 (for Cr\textsuperscript{3+}) or 6.0 (for Cd\textsuperscript{2+}).

The maximum removal rates of Cr\textsuperscript{3+} and Cd\textsuperscript{2+} increased with increasing the initial concentrations of Cr\textsuperscript{3+} and Cd\textsuperscript{2+} and a greater dosage of XCTS was required for higher concentration of metal ions. For the water samples of these two metal ions, the removal rates all increased gradually with increasing XCTS dosage at the beginning until the dosage reached a certain threshold amount. After that, the removal rates all tended to decrease gradually with increasing XCTS dosage. We can achieve the optimum dosages of XCTS and the maximum removal rates for different metal ions at each initial concentration. For example, when the initial concentration of Cr\textsuperscript{3+} was 5, 15, 25 and 50 mg·L\textsuperscript{-1}, the optimum dosage of XCTS was 120, 240, 360 and 420 mg·L\textsuperscript{-1}, respectively; the corresponding removal rate was 71.3%, 92.1%, 98.8% and 98.6%, respectively. For the water samples containing Cr\textsuperscript{3+} with initial concentrations of 5, 15, 25 and 50 mg·L\textsuperscript{-1}, the molar ratio of XCTS to Cr\textsuperscript{3+} in solution at a maximum removal rate was calculated as 3.6:1, 2.4:1, 2.2:1 and 1.3:1. The molar ratio of XCTS to Cr\textsuperscript{3+} significantly decreased with increasing initial concentration of Cr\textsuperscript{3+}, which should be attributed to the adsorption, net capture and sweep action of XCTS. When the number of Cr\textsuperscript{3+} ions in the solution was lower, the collision probability between XCTS and Cr\textsuperscript{3+} was also smaller, and it was difficult for XCTS to play its role in adsorption, net capture and sweep action of XCTS. When the number of Cr\textsuperscript{3+} ions in the solution was lower, the collision probability between XCTS and Cr\textsuperscript{3+} (a chromium ion might combine with three –OCSS\textsuperscript{-} groups from different molecule chains to form reticular flocs, as shown in Figure 3) (Chang & Wang 2007; Chang et al. 2008; Yang et al. 2018). Therefore, a mass of flocs with three-dimensional reticular structure was formed, and rapidly precipitated by gravity. Many microscale chelate precipitates were removed as a result of being rolled into the net, and some Cr\textsuperscript{3+} ions were absorbed by the sinking flocs, which resulted in a decrease in the molar ratios of –OCSS\textsuperscript{-} to Cr\textsuperscript{3+} and an increase in the chromium removal rate. However, the removal efficiency of Cr\textsuperscript{3+} decreased when the XCTS dosage exceeded the optimum dosage because a large number of xanthogenate groups with negative charges accumulated around the flocs under the action of a high concentration of XCTS. These charges, in turn, increased repulsion among the micro flocs, thereby inhibiting the formation of larger flocs (Wang et al. 2013; López-Maldonad et al. 2017). Many micro flocs remained in the supernatant, which led to a decrease in the removal efficiency of metal ions. At dosages larger than a certain molar ratio of –OCSS\textsuperscript{-} to Cr\textsuperscript{3+}, no flocs appeared. The removal mechanism of Cd\textsuperscript{2+} was similar to that of Cr\textsuperscript{3+}, except that each Cd\textsuperscript{2+} combined with two –OCSS\textsuperscript{-} which might come from the same or different XCTS molecules, forming a network structure less obvious than that of Cr\textsuperscript{3+}.

**Comparison of the removal efficiency of Cr\textsuperscript{3+}, Cu\textsuperscript{2+} and Cd\textsuperscript{2+}**

To further investigate the selectivity of XCTS to heavy metal ions, Cr\textsuperscript{3+}, Cu\textsuperscript{2+} and Cd\textsuperscript{2+} were selected as test objects because they were hard acids, boundary acids and soft acids in turn. By comparing the removal rates of the three metal ions and discussing the action mechanism of XCTS on metal ions, it could even be possible to speculate whether XCTS could effectively remove other metal ions.
The mixed simulated wastewater containing 25 mg·L⁻¹ Cr³⁺, Cu²⁺ and Cd²⁺ was used as samples for flocculation tests at an initial pH of 4.0 or 6.0. The removal rates of Cr³⁺, Cu²⁺ and Cd²⁺ in mixed component water samples were compared to that in single component water samples as follows.

Table 1 shows that better removal rates were achieved when XCTS was applied in the treatment of a mixed metal ions solution; the maximum removal rates of Cr³⁺, Cu²⁺ and Cd²⁺ from a mixed component solution were all greater than those of Cr³⁺, Cu²⁺ and Cd²⁺ from a single component solution. When the pH value was 4.0, the maximum removal rates of Cr³⁺, Cu²⁺ and Cd²⁺ were 98.8%, 70.0% (Yang et al. 2018) and 56.6% for the single component solution, and 100%, 100% and 98.0% for the mixed component solution. The maximum removal rates of Cu²⁺ and Cd²⁺ have been greatly improved in a mixed component solution. Similarly, when the pH value was 6.0, the maximum removal rates of Cr³⁺, Cu²⁺ and Cd²⁺ were 92.3%, 92.4% (Yang et al. 2018) and 65.1% for the single component solution, and 100%, 100% and 99.1% for the mixed component solution. Furthermore, when the removal rate of Cr³⁺ reached 100% in the mixed component solution, the dose of XCTS was lower than that in the single component solution. This means that the removal effect of metal ions in the mixed component solution is better than that in the single component solution. Therefore, there was a cooperative removal effect of metal ions in the mixed component solution. In the systems with a mixed component, as the total number of metal ions increased, large amounts of flocs quickly formed and coagulated in water samples when XCTS was added, some of the micro flocs were swept by the big sinking flocs, and a certain number of free metal ions were removed by adsorption. These mechanisms greatly promoted the removal rates of metal ions. As shown in Table 1 and Figure 4, XCTS was selective for the chelation removal of the above metal ions. According to the calculation, when the dosage of XCTS is less than or

Table 1 | Removal rates of Cr³⁺, Cu²⁺ and Cd²⁺ at 25 mg·L⁻¹ in (a) single component water samples and (b) mixed component water samples

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Cr³⁺</th>
<th>Cu²⁺</th>
<th>Cd²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>4.0</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>(a) The optimum dosage (mg·L⁻¹)</td>
<td>360</td>
<td>120</td>
<td>180</td>
</tr>
<tr>
<td>The maximum removal rate (%)</td>
<td>98.8%</td>
<td>70.0%</td>
<td>56.6%</td>
</tr>
<tr>
<td>Residual concentration (mg·L⁻¹)</td>
<td>0.295</td>
<td>7.498</td>
<td>10.848</td>
</tr>
<tr>
<td>(b) The optimum dosage (mg·L⁻¹)</td>
<td>300</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>The maximum removal rate (%)</td>
<td>92.3%</td>
<td>92.4%</td>
<td>65.1%</td>
</tr>
<tr>
<td>Residual concentration (mg·L⁻¹)</td>
<td>1.920</td>
<td>1.895</td>
<td>8.730</td>
</tr>
<tr>
<td>(a) The optimum dosage (mg·L⁻¹)</td>
<td>120</td>
<td>300</td>
<td>720</td>
</tr>
<tr>
<td>The maximum removal rate (%)</td>
<td>100%</td>
<td>100%</td>
<td>99.1%</td>
</tr>
<tr>
<td>Residual concentration (mg·L⁻¹)</td>
<td>0.228</td>
<td>6.0</td>
<td></td>
</tr>
</tbody>
</table>
equal to 240 mg·L⁻¹⁻¹, the average ratio of removal rate with Cr³⁺, Cu²⁺ and Cd²⁺ is 1:1:0.53 at pH 4.0 and 1:0.99:0.79 at pH 6.0, indicating that XCTS has similar and better chelation selectivity to Cr³⁺ and Cu²⁺, while the selectivity for Cd²⁺ is obviously weak (Bonilla-Petriciolet et al. 2019).

According to the hard/soft-acid/base principle, hard acids prefer binding to hard bases, soft acids prefer binding to soft bases, borderline acids/bases can react both with bases and acids whether hard or soft; the compounds formed by boundary acids or bases are just less stable than those formed by hard acids and hard bases or soft acids and soft bases (Pearson 1968; Pearson 1990). In our experiment, Cr³⁺ is a hard acid, Cu²⁺ is a borderline acid and Cd²⁺ is a soft acid. In general, organic sulfide is a soft base, such as RS⁻, SCN⁻ and S₂O₃²⁻. The dithiocarboxy group (–CSS⁻) with strong affinity to heavy metals is also a soft base because it is more likely to bind to soft acids (Liu et al. 2013; Bediako et al. 2015). If the xanthogenate group (–OCSS⁻) is soft, it should prefer to chelate with Cd²⁺. However, the opposite is true. Therefore, we boldly speculate that –OCSS⁻ may be a hard base. It is well known that whether a Lewis base is soft or hard is determined by the ability of a donor to give electrons. The stronger the ability of a donor to give electrons, the harder the base is; whereas the weaker the ability, the softer the base is (Hancock & Martell 1996). Compared with –CSS⁻, due to the p-π conjugate formed by the lone pair electrons on the oxygen atom and bond of C=S, the electron can move in the direction of a double bond which produces the electron conjugate effect, enhances the ability of a donor to give electrons of –OCSS⁻ and leads to the enhanced alkaline. Although the oxygen atom is more electronegative, has a strong ability to absorb electrons, and can produce an induction effect in bonds, the conjugate effect on the properties of organic compounds is often more influential than the induction effect. Therefore, the alkaline of the xanthogenate group is stronger than that of the dithiocarboxy group. It is possible that the –OCSS⁻ group is a hard base. This implies that the heavy metal ions in wastewater, which belong to hard acids, are more easily removed by XCTS.

The removal of Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ by XCTS

Based on our previous research and the inference that the heavy metal ions belonging to hard acids are more easily removed by XCTS, it was estimated that XCTS would have a good removal efficiency for some heavy metal ions belonging to hard acids or borderline acids. To verify our inference, single component water samples containing Mn²⁺, Ni²⁺, Pb²⁺ or Zn²⁺ were used at initial concentration of 25 mg·L⁻¹ with an initial pH 6.0 (Chang & Wang 2007; Liang et al. 2010). Flocculation tests were conducted at different XCTS doses which varied from 60 to 540 mg·L⁻¹. The results are shown in Figure 5.

Figure 5 shows that the maximum removal rates of Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ were 99.9%, 99.7%, 95.0% and 98.5%, respectively. As expected, XCTS could remove Mn²⁺ effectively and the removal rate of Mn²⁺ was highest.

Figure 4 | Removal rates of Cr³⁺, Cu²⁺ and Cd²⁺ from their mixture at (a) pH 4.0 or (b) pH 6.0.

Figure 5 | Removal of Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺ by XCTS from single component water samples.
among the above four kinds of heavy metal ions. Because Mn$^{2+}$ belonged to hard acids, our inference that the metal ions belonging to hard acids are more easily removed by XCTS was further supported. Moreover, XCTS also had good removal effect on Ni$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ which belonged to borderline acids. It means that XCTS possesses a great potential for practical application.

**Flocs characterization**

**Structure of the XCTS–metal ion complex**

FTIR spectroscopy is an effective tool to characterize flocs and confirm the chelation of XCTS and heavy metal. The IR spectra of XCTS, XCTS-Cr and XCTS-Cd are shown in Figure 6.

The spectra exhibited many changes after Cr$^{3+}$ chelation and Cd$^{2+}$ chelation, but the main changes were almost identical to Cu$^{2+}$ chelation (Yang et al. 2018). Compared with Figure 6(a), the original strong absorption peak at 1,446 cm$^{-1}$, which can be assigned to the stretching vibrations of C=S groups, was significantly weakened and split into two absorption peaks at 1,451 cm$^{-1}$ and 1,376 cm$^{-1}$ after Cr$^{3+}$ chelation and Cd$^{2+}$ chelation. The original absorption band at 879 cm$^{-1}$ in Figure 6(a), which can be attributed to the bending vibrations of C-S, was weakened and shifted to 869 cm$^{-1}$ after chelation. In contrast, the original absorption peak at 1,022 cm$^{-1}$, which can be assigned to the stretching vibrations of C-S groups, was significantly strengthened after chelation. Two new strong absorption peaks at 1,196 cm$^{-1}$ and 1,121 cm$^{-1}$, which can be attributed to the stretching vibrations of C-S groups, appeared in the spectra of the XCTS-metal ion complex. This may be due to the splitting of the stretching vibrations peak of C-S groups at 1,155 cm$^{-1}$ (Chang et al. 2008; Liu et al. 2013). These results demonstrated that the C=S groups and C-S groups both participated in a chelation process that affected the molecular structure (Yang et al. 2018). This was also consistent with the mechanism of chelation between XCTS and Cr$^{3+}$/Cd$^{2+}$.

**Morphology of the flocs**

Scanning electron microscopy (SEM) images of the flocs from the flocculation experiments at the optimum dosage of XCTS are shown in Figure 7.

As shown in Figure 7, the sizes of the flocs of XCTS-Cr and XCTS-Cu were significantly greater than that of XCTS-Cd. Furthermore, the XCTS-Cr flocs were visibly honeycombed. This indicated that net capture and sweep were the predominant mechanism for the removal of Cr$^{3+}$. The XCTS-Cu flocs appeared relatively compact. The XCTS-Cd flocs were finely granular; it was hard to find larger size of flocs. The results indicated that the structure, morphology and particle size of flocs were closely related to the removal of heavy metal ions. However, overall, the morphologies of the flocs (XCTS-Cr, XCTS-Cu and XCTS-Cd) were irregular and showed obvious signs of adhesion and aggregation, which indicated that the flocs were linked to each other and accumulated to form larger flocs. Therefore, the interparticle bridging mechanism plays a major role in the formation of flocs.

**CONCLUSION**

XCTS possesses not only strong chelating abilities toward heavy metal ions but also excellent flocculation properties. Outstanding effects can be obtained for acidic wastewater. The optimal dosage is related to the pH of the solution and the initial concentration of metal ions. The −OCSS− group on the molecular chain of XCTS plays a key role in the chelating and flocculating process towards heavy metal ions and the huddling process of flocs. By comparison, it was found that the removal rates of Cr$^{3+}$ (98.8% and 100%) were much higher than those of Cd$^{2+}$ (65.1% and 99.1%) in both single component solution and mixed component solution, respectively.

![Figure 6](https://iwaponline.com/wst/article-pdf/79/12/2289/595953/wst079122289.pdf)
The result showed that the XCTS was easier to combine with the heavy metal ions belonging to hard acids. The removal of Mn\(^{2+}\) by XCTS further verified this inference. The maximum removal rate of Mn\(^{2+}\) reached 99.9%. Moreover, when using XCTS the removal rates of Ni\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) could reach 99.7%, 95.0% and 98.5%, respectively. Therefore, XCTS has a good potential for practical application.

ACKNOWLEDGEMENTS

This research was supported by the National Nature Science Foundation of China (Grant No. 51368030).

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First received 14 February 2019; accepted in revised form 29 June 2019. Available online 8 July 2019.