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Preparation and performance of CTS-AM-ETA as a modified chitosan flocculant

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ABSTRACT

Flocculation is often an important method for removing colloids from water or wastewater to obtain excellent water quality before advanced treatment. Flocculation efficiency largely depends on the flocculant used. A modified chitosan flocculant, named CTS-AM-ETA, was successfully prepared by modifying chitosan (CTS) with acrylamide (AM) and 2,3-epoxypropyl trimethyl ammonium chloride (ETA) for improved removal of lignin and cellulose-generated organic loads from papermaking wastewater in this study. The flocculation performance of CTS-AM-ETA was compared with chitosan and traditional inorganic flocculants. Compared with CTS, the results of Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and solution properties showed that the composition, structure and morphology of CTS-AM-ETA had changed, which resulted in the improvements in adsorption, bridging and electrical neutralization of the flocculant by increasing the specific surface area, the molecular weight and the cation strength. The turbidity and chemical oxygen demand removal indicated that the flocculation performance of CTS-AM-ETA was superior to chitosan and the selected inorganic flocculants under optimal dosage conditions. The larger particle size of the sludge flocs by CTS-AM-ETA could promote the sweeping and deposition of aggregates. In particular, preliminary results found the sludge flocs could adsorb the cationic dye methylene blue.

Keywords: Chitosan; Acrylamide; 2,3-Epoxypropyl trimethyl ammonium chloride; Papermaking wastewater; Methylene blue

1. Introduction

The paper industry is one of the largest industrial production sectors. A large amount of wastewater is generated in the paper industry. In China, papermaking wastewater industry discharges about 2.367 billion tons wastewater per year, accounting for 13.0% of the country's total industrial wastewater discharge, and ranking the first among 41 industries [1,2]. In addition to the large amount of wastewater, papermaking wastewater contains a variety of refractory organic substances (lignin, cellulose and hemicellulose etc.), and the percentage of lignin and cellulose in the influent chemical oxygen demand (COD) exceeds 80% [3]. Once the pollutants in papermaking wastewater are directly discharged, they will destroy the aquatic community and reduce the river's self-purification ability.

At present, the main methods in industrial treatment for papermaking wastewater include biological treatment, chemical oxidation, adsorption, membrane separation, flocculation, etc. [4–9]. Compared with other treatment methods,

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flocculation has the advantages of simple method, short time, low cost, and high efficiency [10]. In the previous flocculation treatment, traditional inorganic flocculants and synthetic polymer flocculants have been used as the most conventional flocculant. However, the disadvantages of these flocculants have emerged with the continuous in-depth research and application. Generally, traditional inorganic flocculants can no longer meet people's water quality needs; while synthetic polymer flocculants are expensive and not easily degraded. Therefore, more and more attention has been paid to the natural polymer flocculants that are not harmful to the environment and are biodegradable. Chitosan derived from the carapace of aquatic crustaceans, is one of the natural flocculants. Chitosan is a soluble cationic polymer with high charge density and long polymer chains under acidic conditions (below pH = 5), which can effectively neutralize and bridge the contaminants in the suspended and dissolved state [11–14]. In addition, chitosan contains amino, N-acetyl and hydroxyl groups, so chitosan can be easily modified to meet various applications by introducing different functional groups on the chitosan skeleton [10,15].

Previous studies have shown that chitosan has a significant flocculation effect as a natural flocculant. Patel and Vashi [16] used chitosan as a flocculant for the removal of Congo red in textile printing and dyeing wastewater. The results showed that the maximum removal percentage of Congo red by chitosan was 94.5% under the conditions of pH = 4.0, flocculant dosage 25 mg/L, flocculation time 60 min, and temperature 340 K. Gassara et al. [17] proved that both chitin and chitosan had the ability to flocculate colloidal particles in beer. Among all the flocculants tested, chitosan was found to be the most effective and superior to conventional flocculants in beer clarification at both laboratory scale and industrial scale. Ji et al. [18,19] pretreated domestic sewage with chitosan and traditional flocculants, and combined with membrane bioreactor to explore the effects of different flocculants on membrane fouling. The results showed that membrane bioreactor pretreated with chitosan flocculant guaranteed high effluent water quality and had the least degree of membrane fouling. Feng et al. [20] studied the flocculation effect of chitosan flocculant on quartz wastewater under different pH values. The results showed that chitosan had a good removal effect on quartz wastewater. Wu et al. [21] used chitosan flocculant to treat wastewater rich in manganese ions and suspended solids. The results showed that chitosan flocculant had a strong removal effect on manganese ions and suspended solids.

Based on the characteristics of non-toxic, harmless and friendly to the environment, chitosan is usually modified to further improve its flocculation performance. The increase in the molecular weight of chitosan can improve the adsorption and bridging effects during the flocculation process. Hermosillo-Ochoa et al. [22] grafted chitosan, polyvinyl caprolactam and polyacrylic acid to treat chromium-containing wastewater, and the removal rate of chromium ions could reach 95%. Sun et al. [23] grafted chitosan, acrylamide, and ammonium dithiocarbamate by UV initiation, and used the flocculant to treat nickel in power plant wastewater. The quality of the effluent was 0.96 mg/L of nickel ion concentration, 93 mg/L of COD, and 1.71 NTU of turbidity under optimal conditions. Sun et al. [24] grafted carboxymethyl chitosan, polyacrylamide, and sodium coxanthate by UV-initiated method. The removal rate of Cu, Cr, and Ni could reach 85.1%, 76.1% and 75.7% by using the flocculant, respectively. Tang et al. [25] prepared a sulfonated chitosan flocculant and used it to treat heavy metals in hematite wastewater. The flocculant was grafted with acrylamide on the basis of the sulfonation reaction of chitosan, so the molecule contained a large number of groups were beneficial to the removal of heavy metal ions and improved the flocculation performance. Zeng et al. [26] synthesized a new type of flocculant from chitosan and dextran by microwave thermal initiation, and proved the successful grafting through a variety of characterization methods. The kaolin suspended particles were treated with the flocculant, and the turbidity removal rate was 93.6%.

The increase in the cationic strength of chitosan can also improve the flocculation efficiency by increasing the charge neutralization. Li et al. [27] prepared an amphoteric flocculant from cationic chitosan and anionic polyglutamic acid, and used the flocculant to treat starch wastewater. When the dosage was 80 mg/L, the removal rates of COD, ammonia nitrogen, total phosphorus and turbidity were 44.8%, 53.4%, 28.1% and 98.1%, respectively. Feng et al. [28] grafted chitosan, acrylamide, and 3-acrylamidopropyl trimethyl ammonium chloride by means of ultrasonic initiation, and explored the factors affecting the grafting rate and grafting efficiency. The best removal rate could reach 91.9% when treating acidic blue aqueous solution with the agent.

In order to improve the removal of organic loads generated by lignin and cellulose in papermaking wastewater, CTS-AM-ETA was prepared by modifying chitosan with acrylamide (AM) and 2,3-epoxypropyl trimethyl ammonium chloride (ETA) in this study. The material properties and flocculation performance of CTS-AM-ETA were studied, especially the sludge flocs generated from CTS-AM-ETA were preliminarily explored as adsorbents.

2. Materials and methods

The experiment was divided into three stages.

To successfully prepare CTS-AM-ETA, a two-step method was used to modify the amino group and molecular side chain of chitosan by AM and ETA in the first stage. Furthermore, the structure, composition, morphology and solution properties of CTS-AM-ETA were characterized.

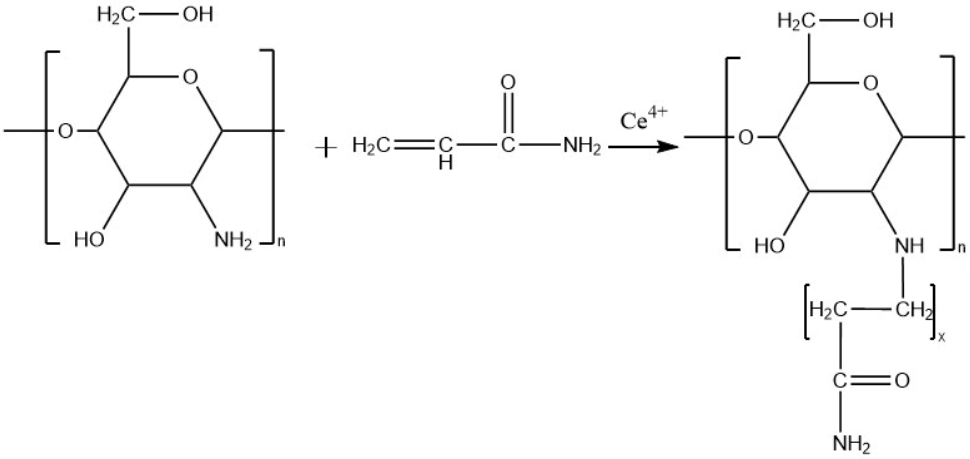
Based on the results of the first stage, jar-test were performed in the second stage to investigate the flocculation performance of CTS-AM-ETA. In order to get accurate results, synthetic papermaking wastewater was used throughout the experimental stage. The removal rate and residual concentration of turbidity and COD were mainly detected and compared with the existing traditional inorganic flocculants. Sludge flocs produced by CTS-AM-ETA were tested for size distribution to investigate their potential settleability and practicality.

In the third stage, static adsorption experiments were designed and investigated the effects of sludge floc dosage, time and temperature on the adsorption effect of methylene blue, in order to explore the possibility of sludge flocs as adsorbents to treat the cationic dye methylene blue in printing and dyeing wastewater.

2.1. Preparation of CTS-AM and CTS-AM-ETA

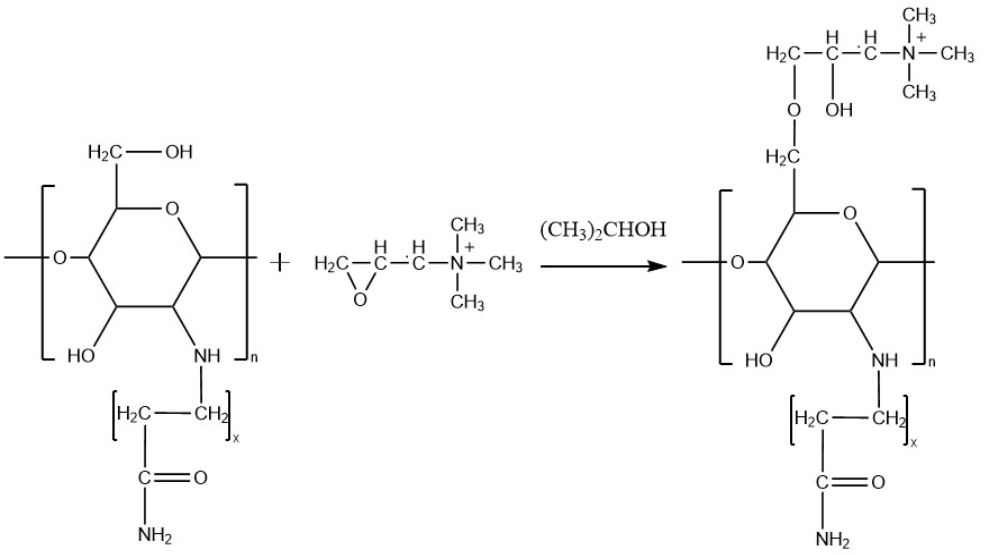
2.1.1. Preparation of CTS-AM

First of all, 1 g chitosan (CTS) was dissolved in 100 mL of 3% glacial acetic acid in a three-necked flask. Cerium ammonium nitrate at a concentration of 8 mmol/L was added as an initiator to the three-necked flask blown with argon to completely remove air. Secondly, 4 g of AM was added to the three-necked flask to react with CTS for 3.5 h at 35°C, and then the mixture was cooled to room temperature and adjusted to pH = 7 with 1 mol/L NaOH. At last, the mixture was added with 50 mL of acetone and centrifuged at 4,500 rpm for 5 min to obtain a solid product. The solid product was placed in a Soxhlet extractor containing 150 mL of acetone and extracted for 48 h to remove unreacted reactants. The extract was dried for 12 h at 40°C to obtain CTS-AM. The reaction for preparing CTS-AM is shown:



2.1.2. Preparation of CTS-AM-ETA

1 g of the prepared CTS-AM was dissolved in 100 mL of 3% glacial acetic acid solution, which was placed in a three-necked flask. Argon as a protective gas was fed into the three-necked flask, which was connected to a condensing reflux device. 3 g of ETA and 50 mL of isopropanol as etherifying agent were added to the three-necked flask and reacted with the prepared CTS-AM for 16 h at 85°C, and then the mixture was cooled to room temperature and adjusted to pH = 7 with 1 mol/L NaOH. The mixture was added with 50 mL of acetone and centrifuged at 4,500 rpm for 5 min to obtain a solid product. The solid product was placed in a Soxhlet extractor containing 150 mL of acetone and extracted for 24 h to remove unreacted reactants. The extract was dried for 12 h at 40°C to obtain CTS-AM-ETA. The reaction for preparing CTS-AM-ETA is shown:



CTS, glacial acetic acid, cerium ammonium nitrate, AM, NaOH, acetone, ETA, isopropanol were analytical reagents in this work. Argon was high purity.

2.2. Jar-test

A synthetic papermaking wastewater comprising of sodium lignosulfonate, cellulose, hemicellulose and sodium humate as dominant pollutants was used throughout the experimental period. The quality of the synthetic papermaking wastewater was turbidity of 176 NTU and COD of 814 mg/L. According to [3,29], the proportion of COD provided by the main pollutants in synthetic papermaking wastewater is listed in Table 1.

In order to compare the flocculation effect of CTS-AM-ETA with traditional flocculants on papermaking wastewater, jar-test was performed with rapid mixing at 120 rpm (perikinetic phase) for 3 min, slow mixing at 30 rpm (orthokinetic phase) for 15 min, and a settling phase for 30 min. Aluminum sulfate, polyferric sulfate and polyaluminum chloride were purchased in the local market as traditional inorganic flocculants. Stock solutions of aluminum sulfate, polyferric sulfate and polyaluminum chloride were prepared by dissolving the reagents in deionised water at a concentration of 10 g/L, respectively. Stock solutions of CTS, CTS-AM and CTS-AM-ETA were 1 g/L respectively.

2.3. Static adsorption experiment

The sedimentation process after flocculation can realize the separation of effluent and sludge flocs in papermaking wastewater. Those sludge flocs containing substances such as lignin and cellulose are pollutants with higher moisture content. At present, the treatment method of sludge flocs generated from papermaking wastewater is dehydration and then landfilling in industry, but that undoubtedly causes a waste of resources. Therefore, this work tried to use the sludge flocs as adsorbents for the treatment of methylene blue which exists in printing and dyeing wastewater as a typical cationic dye.

The sludge flocs generated by CTS-AM and CTS-AM-ETA were filtered and dried to explore the adsorption effect on methylene blue. A series of stoppered conical flasks containing sludge flocs (0.2–1 g) and 100 mL of 50 mg/L methylene blue solution (pH = 6.58) were placed in a water bath shaker. The water bath shaker was operated at a certain temperature and for a certain period of time. The residual concentration of the methylene blue solution was tested to calculate the removal efficiency after adsorption.

Table 1
COD percentage of the main pollutants in synthetic papermaking wastewater

Composition	COD
Sodium lignosulfonate	27.02%
Cellulose	50.49%
Hemicellulose	14.3%
Other	8.19%

2.4. Methods of analysis

In order to analyze the changes in the composition, structure and morphology, the flocculants were characterized by Fourier-transform infrared spectroscopy (FT-IR) (Spectrum Two, Perkin Elmer), X-ray diffraction (XRD) spectrum analysis (Escalab 250Xi, Thermo Scientific) and scanning electron microscopy (SEM) (S-3400N, FEI). The zeta potential of the flocculants with pH value were analyzed by Zetasizer (Nano90, British Malvern Company). The viscosity of the flocculants in a 3% glacial acetic acid solution was tested by digital viscometer (NDJ-8S, China Shanghai Gaozhi Precision Instrument Co., Ltd.). The size distribution of sludge flocs generated by the flocculants was characterized by Particle Size Analyzer (BT9300S, China Dandong Better Instruments Co., Ltd.)

In this work, the treatment performance of the flocculants on the synthetic papermaking wastewater was characterized by turbidity and COD. The values of turbidity and COD were obtained by analyzing the supernatant sample with a DR890 colorimeter (HACH, America). The removal efficiency of the sludge flocs was calculated by Eq. (1):

$$Q_R = \frac{\left(C_0 - C_e\right)}{C_0} \times 100\% \quad (1)$$

where Q_R (%) was the removal efficiency. C_0 and C_e referred to the concentration of methylene blue solution (mg/L) at the start of the experiment and at equilibrium, respectively.

3. Results and discussion

3.1. Characterization of the flocculants

3.1.1. FT-IR spectra

Fig. 1 shows the FT-IR spectra of CTS before and after modification. Compared with CTS in Fig. 1a, the N–H bending vibration peak of primary amine disappeared at 1,597 cm^{-1} in CTS-AM. The stretching vibration peaks of C=O

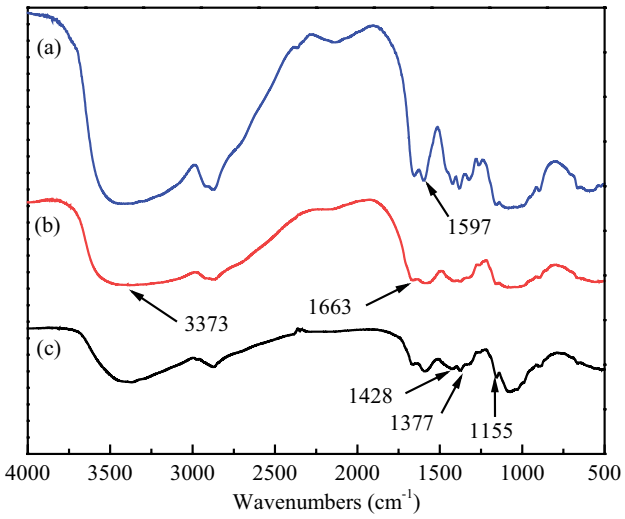


Fig. 1. FT-IR spectra of (a) CTS, (b) CTS-AM and (c) CTS-AM-ETA.

and N–H in amide group appeared at 1,663 and 3,373 cm^{-1} in Fig. 1b, respectively. The results indicated that AM had been successfully grafted onto the amino group of CTS.

Compared with CTS-AM in Fig. 1b, the C–H bending vibration peaks of methyl and methylene appeared at 1,428 and 1,377 cm^{-1} in CTS-AM-ETA of Fig. 1c, respectively. The results could be attributed to the vibration coupling effect that caused the umbrella bending vibration of the methyl group in the quaternary ammonium group to split [30]. The C–O–C asymmetric stretching vibration peak of the ether group appeared at 1,155 cm^{-1} in Fig. 1c, which indicated that the CTS in CTS-AM had an epoxy ring-opening reaction under the action of the etherifying agent, and the quaternary ammonium group was successfully introduced into the CTS molecule side chain in CTS-AM. Based on the above results, CTS-AM-ETA was successfully prepared.

3.1.2. X-ray diffraction

Fig. 2 shows the XRD analysis of CTS and its derivatives. In Fig. 2a, the strong diffraction peak at 20.3° indicated the crystal structure of CTS due to its strong hydrogen bonding.

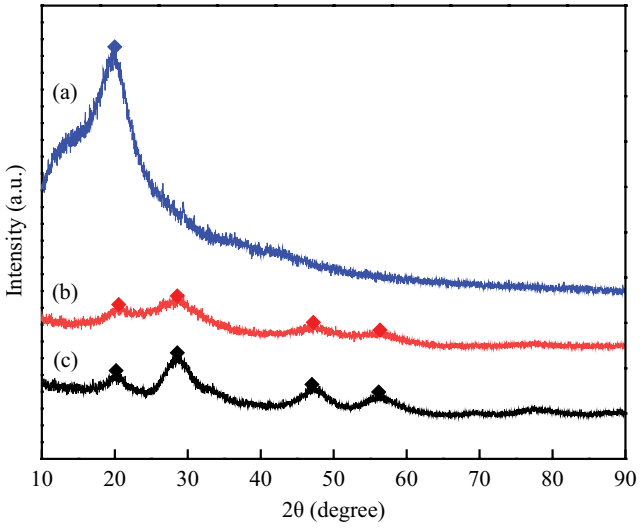


Fig. 2. XRD analysis of of (a) CTS, (b) CTS-AM and (c) CTS-AM-ETA.

When AM was grafted to the amino position of CTS, the intramolecular and intermolecular hydrogen bonds were destroyed and the diffraction peak was shifted. That is, the diffraction peaks of CTS-AM at 20.3° was greatly reduced in Fig. 2b, while weaker diffraction peaks appeared at 23.68°, 47.24°, and 55.92°. The results meant that the crystallinity of CTS-AM was reduced, which was beneficial to improve its solubility in water or organic solvents [31,32].

In Fig. 2c, the position of the diffraction peak in CTS-AM-ETA was consistent with that in CTS-AM, but the intensity of the diffraction peak was slightly enhanced. This could be attributed to the fact that the introduction of ETA increased the number of quaternary ammonium groups, and the effect of ions changed the short-range arrangement of CTS, resulting in better crystal characteristics of CTS-AM-ETA [33].

3.1.3. SEM image

The smooth, less porous, and dense surface in Fig. 3a, indicated that CTS had a compact crystal structure due to the existence of intramolecular and intermolecular hydrogen bonds.

When the amino position of CTS was grafted by AM, the intramolecular and intermolecular hydrogen bonds were destroyed and the crystal structure collapsed, showing the loose, porous and rough surface of CTS-AM in Fig. 3b. This change in the surface morphology was conducive to increasing the specific surface area and the adsorption role of the flocculant, and improving the flocculation performance [31].

The introduction of ETA further destroyed the hydrogen bond of CTS, thus the surface of CTS-AM-ETA was more loose, porous and rough than that of CTS-AM in Fig. 3c. The results indicated that the specific surface area and the adsorption role of the flocculant would be further enhanced.

3.1.4. Solubility

The changes in crystal properties and the introduction of quaternary ammonium groups may affect the solubility of the flocculant, so the water solubility of flocculants at different pH values was qualitatively tested in this work.

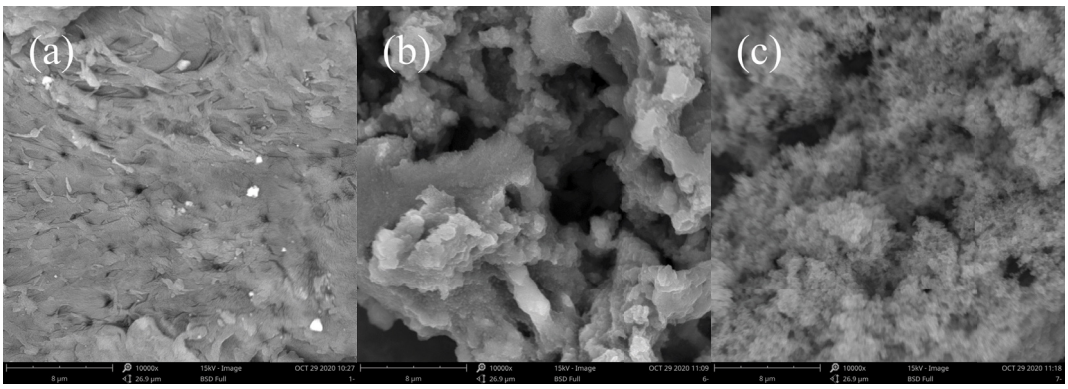


Fig. 3. SEM images of (a) CTS, (b) CTS-AM and (c) CTS-AM-ETA.

Table 2 represents that the pH value affected the water solubility of the flocculant. Acidic conditions were conducive to the dissolution of the flocculants, and the increase in pH reduced the solubility of the flocculants. The dissolution pH range of the flocculant was CTS, CTS-AM and CTS-AM-ETA from narrow to wide. The results illustrated that the grafted AM destroyed the crystal structure of CTS and increased the solubility of CTS-AM. Moreover, the introduction of ETA not only destroyed the crystal structure of CTS, but also increased the hydrophilicity due to the quaternary ammonium groups group [34]. Therefore, the modified CTS expanded the application range of pH value and improved the practicality of the flocculant in actual wastewater.

3.1.5. Zeta potential

The improvement of solubility may affect the cation strength and electric neutralization of the flocculants, so the zeta potential of the flocculants in deionized water was tested.

Fig. 4 shows that the order of zeta potential from strong to weak was CTS-AM-ETA, CTS-AM and CTS in the pH range of 1–12. The results revealed that the modification of CTS increased the zeta potential. Since the sodium lignosulfonate in papermaking wastewater is negatively charged [32], the increase in zeta potential could improve the electric neutralization of the flocculants.

Table 2
Solubility of the flocculants at different pH values

pH \ Flocculants	CTS	CTS-ETA	CTS-ETA-AM
1	F	F	F
2	S	S	F
3	S	S	S
4	I	S	S
5	I	S	S
6	I	S	S
7	I	I	S
8	I	I	S
9	I	I	I
10	I	I	I
11	I	I	I
12	I	I	I

Note: F—Fully soluble, S—Slightly soluble, I—Insoluble

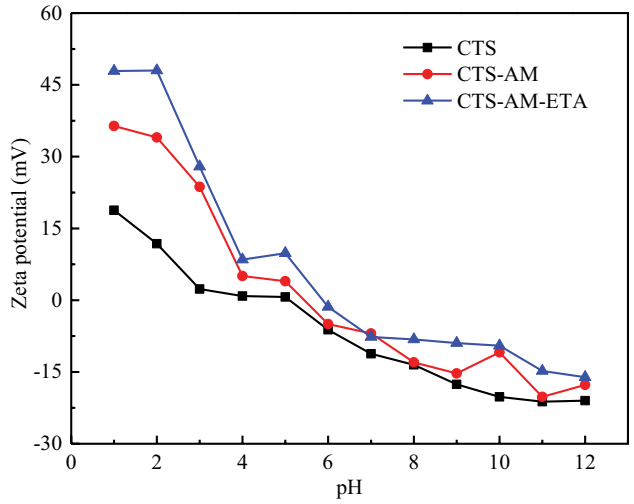


Fig. 4. Zeta potential of the flocculants with pH change.

3.1.6. Viscosity and molecular weight

Fig. 5 shows the viscosity of the flocculants in 3% glacial acetic acid solution. It can be seen that the viscosity of CTS, CTS-AM and CTS-AM-ETA gradually increased. As a measure of molecular weight, the higher the viscosity value, the higher the molecular weight [35,36]. The results implied that the molecular weight of modified CTS gradually increased, which was conducive to the bridging effect of the flocculant [37]. Therefore, the flocculation performance was studied in Section 3.2.

3.2. Flocculation performance of the flocculants

3.2.1. Turbidity and COD removal

Figs. 6 and 7 show the turbidity and COD removal of synthetic papermaking wastewater treated by CTS before and after modification compared to traditional inorganic flocculants. Among the selected inorganic flocculants, polyaluminum chloride had the best treatment performance. When the dosage of polyaluminum chloride was 120 mg/L, the turbidity removal rate was 91% and the residual turbidity was 18 NTU, and the COD removal rate was 77.9% and the residual COD was 180 mg/L.

As modified CTS, the turbidity removal performance and the COD removal performance of CTS-AM and CTS-AM-ETA were higher than that of CTS in the treatment of synthetic papermaking wastewater. The turbidity removal rates of CTS-AM and CTS-AM-ETA were 8.3% and 8.8% higher than the CTS value of 90%, and their COD removal rates were 2.2% and 9.2% higher than the CTS value of

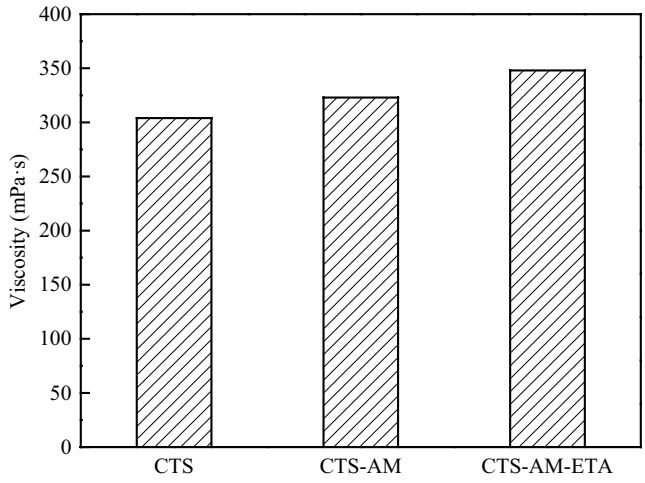


Fig. 5. Viscosity of the flocculants.

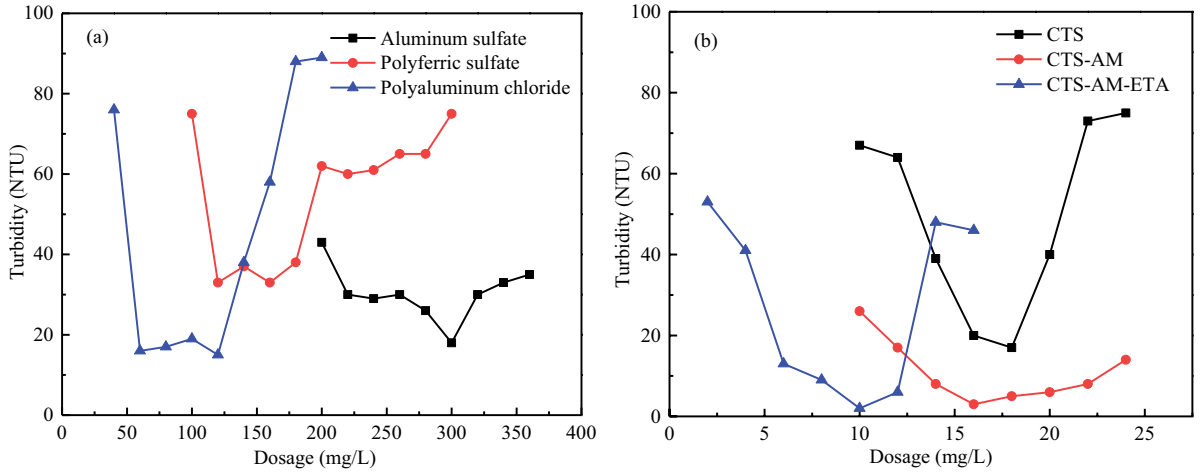


Fig. 6. Variations of turbidity with dosage of the flocculants.

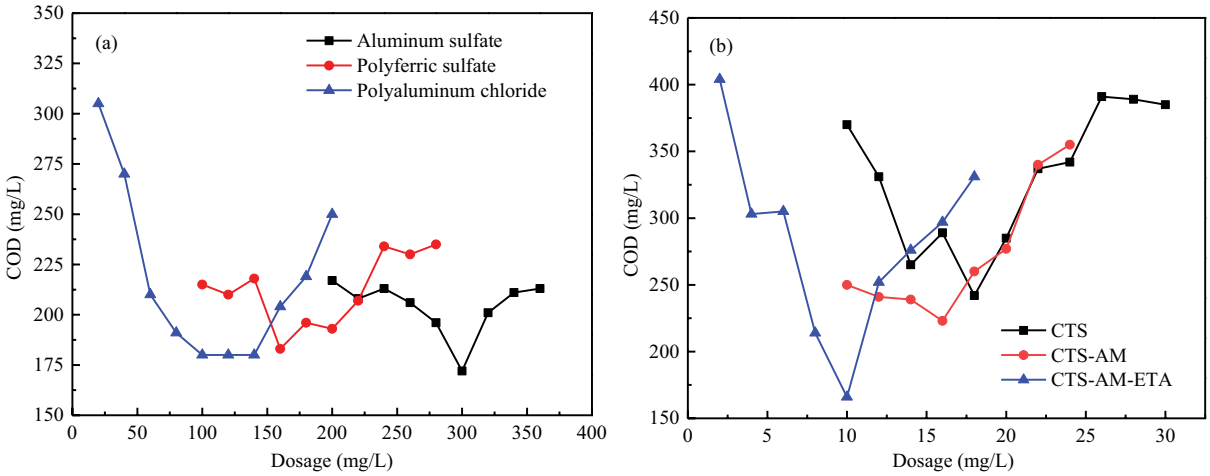


Fig. 7. Changes of COD with dosage of the flocculants.

70.4%, under the optimal dosage conditions. The results were mainly attributable to the increase in specific surface area, molecular weight and cationic strength of the modified CTS, which improved the adsorption, bridging and electric neutralization effect of the flocculants.

The flocculation performance of CTS-AM-ETA was better than that of polyaluminum chloride, and the optimal dosage of CTS-AM-ETA was less than that of polyaluminum chloride. The smaller dosage was convenient for the transportation and storage of the flocculant in the wastewater treatment plant. When the CTS-AM-ETA dosage was 10 mg/L, the turbidity removal rate was 98.8% and the residual turbidity was 2 NTU, and the COD removal rate was 79.6% and the residual COD was 166 mg/L. The residual COD did not meet the limit of 150 mg/L for existing enterprises in the Discharge Standard of Water Pollutant for Pulp and Paper Industry (No. GB3544-2008 in China). Nevertheless, CTS-AM-ETA as a pretreatment could effectively reduce the organic load of the influent in the subsequent advanced treatment process.

3.2.2. Floc size distribution

Fig. 8 shows the particle size distribution of sludge flocs produced by CTS, CTS-AM and CTS-AM-ETA treating papermaking wastewater, respectively. The diff lines in the particle size distribution map refer to the percentage content of the particle size, and the cumu lines refer to the cumulant of the percentage content of all particles before a certain particle size. The median diameter D50 refers to the sludge particle size corresponding to the cumu line when the cumulative particle size content is 50%.

The average particle size of the sludge flocs produced by CTS-AM and CTS-AM-ETA were 44.31 and 49.09 μm, which were higher than the CTS value of 37.26 μm. Moreover, the D50 of the sludge flocs produced by CTS-AM and CTS-AM-ETA were 34.89 and 36.05 μm, which were also higher than the CTS value of 27.55 μm. Larger sludge flocs were beneficial to improve the sweeping effect, and shorten the settling time in the flocculation process [32]. Therefore, the modified CTS was effective and practical for the treatment of actual wastewater.

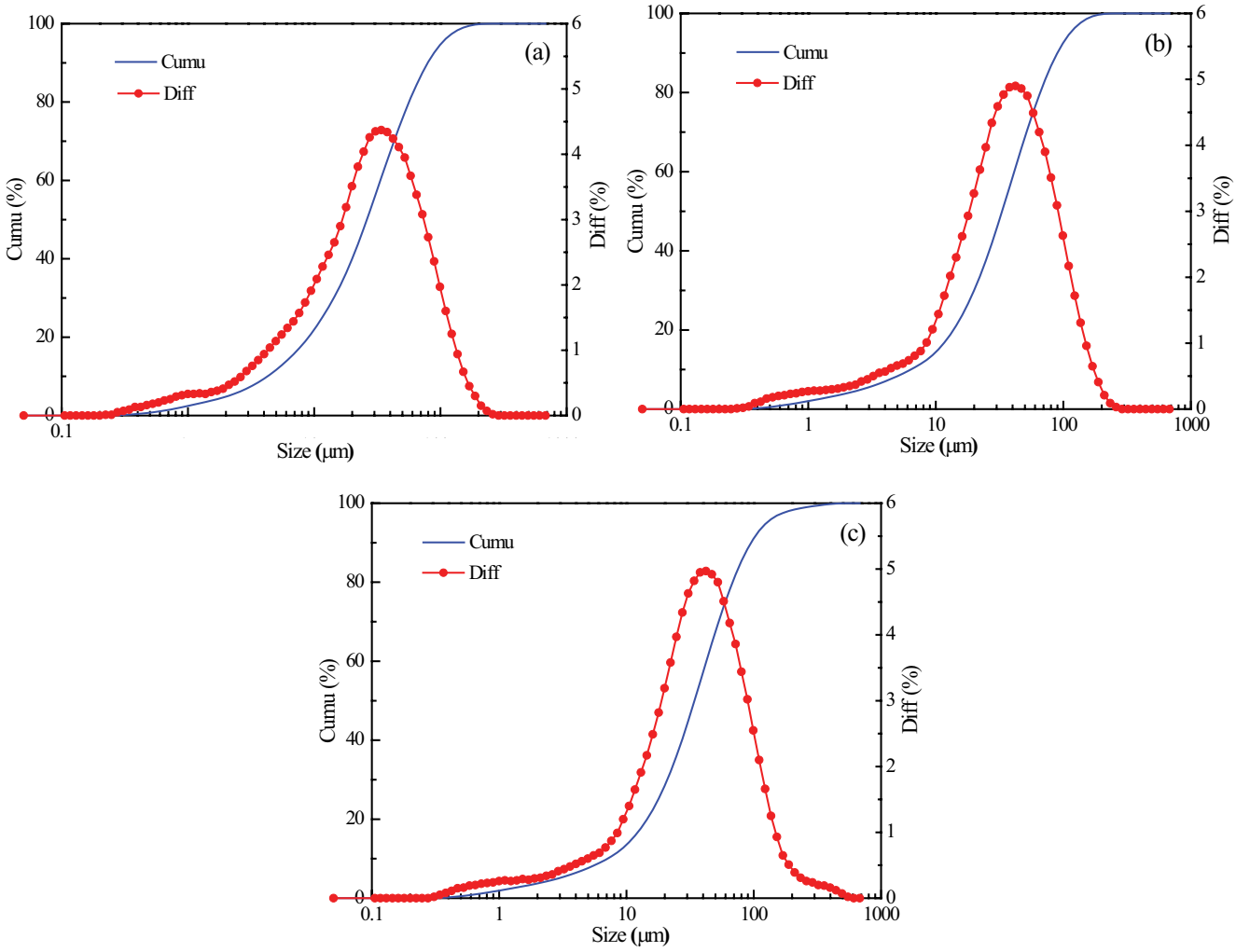


Fig. 8. Particle size distribution of (a) CTS, (b) CTS-AM and (c) CTS-AM-ETA.

3.2.3. *Adsorption possibility of the sludge flocs on methylene blue*

The dosage of the adsorbent is one of the important factors affecting the performance in the adsorption process. Fig. 9a represented that the removal efficiency of methylene blue increased with the increase of the sludge floc dosage until it reached the highest value. When the dosage of sludge floc was less than 6 g/L, the insufficient dosage of adsorbent resulted in undesirable treated water quality. When the sludge floc dosage was higher than 6 g/L, the methylene blue removal efficiency increases slowly, and the excessive dosage would lead to higher operating costs and sludge treatment costs. The optimum dosage, which simultaneously ensured the efficiency and the economy of adsorption, was 6 g/L in this work.

The adsorption time affects the wastewater treatment capacity of the wastewater treatment plant. Fig. 9b shows the evolution of methylene blue removal efficiency over time, when the sludge floc dosage was 6 g/L. The results display that the removal efficiency of methylene blue by sludge flocs could reach more than 90% when the adsorption time was 2 h. After that, the removal efficiency increased with time, but the effect tended to be flat after the time was greater than 6 h. Therefore, the optimum adsorption time in this work was 6 h.

Fig. 9c shows the decrease of the removal efficiency with the increase of temperature, when the sludge floc dosage was 6 g/L and the adsorption time was 6 h. The results demonstrated that the adsorption was an exothermic process [38]. Increasing temperature reduced the adsorption forces between the sludge flocs and the methylene blue, resulting in the decrease in the removal efficiency [38,39]. The value of removal efficiency remained above 97% within the temperature range investigated. Therefore, the optimum temperature should be 20°C in order to save energy in the process.

According to Fig. 9, the removal efficiency of methylene blue reached 99.2%, when the conditions are sludge floc dosage of 6 g/L, adsorption time of 6 h, and adsorption temperature of 20°C. Although the adsorption performance of sludge flocs on methylene blue was excellent, further

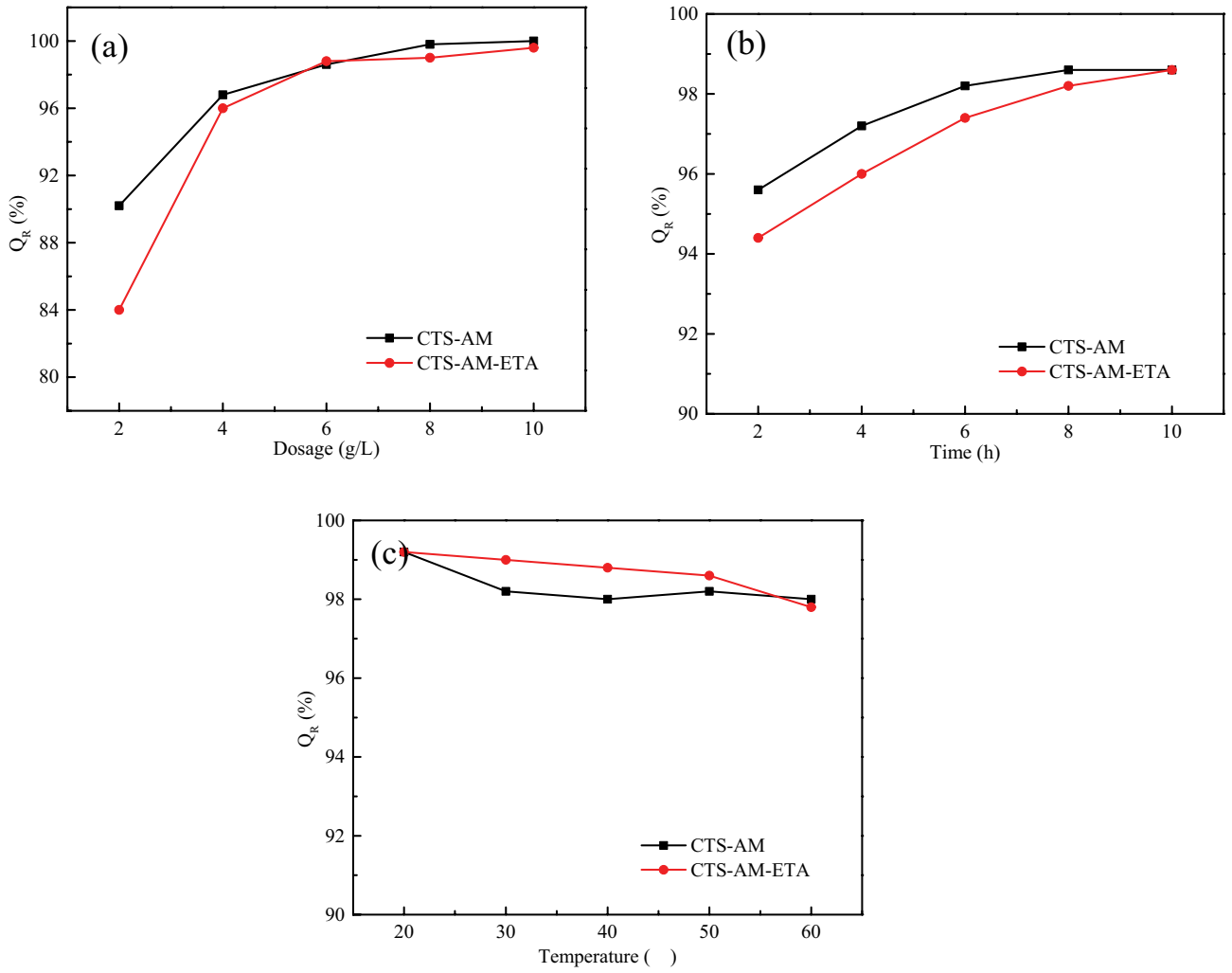


Fig. 9. Effect of (a) dosage of the sludge flocs, (b) adsorption time and (c) temperature on the adsorption performance of methylene blue.

research needs to be explored to investigate the effect of dye type and its concentration on adsorption performance because methylene blue only represented one of the cationic dyes.

4. Conclusions

In this work, FT-IR revealed that CTS-AM-ETA was successfully prepared by grafting AM and ETA onto the amino groups and side chains of CTS. XRD proved that the crystal properties of CTS were destroyed in the modification process, and scanning electron microscopy exhibited that CTS-AM-ETA had a loose, porous and rough surface. The results indicated that CTS-AM-ETA had better adsorption performance than CTS. The water solubility and zeta potential of CTS-AM-ETA were increased compared to the CTS, which was beneficial to broaden the effective range of pH and strengthen the electric neutralization during the flocculation process. The larger molecular weight of CTS-AM-ETA helped to improve the bridging effect of the flocculant. The turbidity and COD removal rate of CTS-AM-ETA had been significantly improved compared to CTS. The optimal dosage of CTS-AM-ETA was less than polyaluminum chloride, but the flocculation performance of CTS-AM-ETA was better than that of polyaluminum chloride. The sludge flocs produced by CTS-AM-ETA had larger particle size, which facilitated the sweeping and netting effects and shorten the settling time of the flocculation process. The removal efficiency of methylene blue reached 99.2%, when the conditions are sludge floc dosage of 6 g/L, adsorption time of 6 h, and adsorption temperature of 20°C.

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