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Cationic content effects of biodegradable amphoteric chitosan-based flocculants on the flocculation properties

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Abstract

A series of biodegradable amphoteric chitosan-based flocculants (3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA) modified carboxymethyl chitosan, denoted as CMC-CTA) with different substitution degrees of CTA were prepared successfully. The content of carboxymethyl groups in each CMC-CTA sample was kept almost constant. The solubility of the various flocculants showed that, higher cationic content of flocculants caused a better solubility. The flocculation experiments using kaolin suspension as synthetic water at the laboratory scale indicated that the substitution degree of CTA was one of the key factors for the flocculation properties. With the increase of cationic content, the flocculants were demonstrated better flocculation performance and lower dosage requirement. Flocculation kinetics model of particles collisions combining zeta potential and turbidity measurements was employed to investigate the effects of the cationic content of the flocculants on the flocculation properties from the viewpoint of flocculation mechanism in detail. Furthermore, flocculation performance using raw water from Zhenjiang part of Yangtze River at the pilot scale showed the similar effects to those at the laboratory scale.

Key words: amphoteric chitosan-based flocculants; substitution degree of CTA; flocculation kinetics and mechanism

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Introduction

Flocculation, an important process for solid-liquid separation (Garcia et al., 2009; Nan et al., 2009), is widely applied in the primary purification of wastewater with suspended particles contamination, due to technological and especially economic reasons (Renault et al., 2009).

Recently, much more attention has been given to research on natural polymer flocculants (Khiari et al., 2010), since they have characteristics of low dosage requirements, low energy input, environmental-friendly, renewable and wide sources (Azlan et al., 2009), which are even acclaimed as “Green Flocculants of 21st Century” (Xiao and Zhou, 2005). Among them, chitosan, poly- β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose, obtained by deacetylation of chitin (the second only less than cellulose in abundance in nature), is one of the most promising candidates, because of its outstanding performance (Chatterjee et al., 2009; Guibal et al., 2006). To date, research of chitosan has become one of the most popular hot aspects (Chatterjee et al., 2009; Guibal et al., 2006).

However, poor solubility under neutral or higher pH conditions always limits the practical application of chi-

tosan. Many researchers have reported that incorporation of other materials can improve this problem. Therein, quaternary modification (Ali and Singh, 2009a; Li et al., 2010; Rojas-Reyna et al., 2010), such as 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA, a kind of low toxic reagent) modified chitosan (Chito-CTA) (Ali and Singh, 2009a; Rojas-Reyna et al., 2010), is usually regarded as an efficient way, which not only widens the solubility range of the flocculants towards neutral and weak alkaline pH, but also benefits for the charge neutralization of negatively charged particles in natural turbid water. Nevertheless, only strengthening cationic degree on chitosan can not improve its solubility at high pH. It is well known that carboxyalkylation is also an efficient way to expand the solubility region of chitosan, especially for high pH region. (Li et al., 2010; Bratskaya et al., 2009; Cai et al., 2007; de Abreu and Campana-Fiho, 2009; Yang et al., 2011a) Therefore, the amphoteric chitosan-based flocculants, containing both anionic and cationic groups, are believed more effective for its wider range of applicability and remarkable increased solubility in the whole pH range.

In our previous work (Yang et al., 2011b), an amphoteric chitosan-based flocculant (CTA modified carboxymethyl

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chitosan, denoted as CMC-CTA), which has notable improvement in solubility and salt-resistance in comparison with chitosan and Chito-CTA, has been successfully prepared. The flocculation experiments both at the laboratory and pilot scale demonstrate that CMC-CTA shows good flocculation performance. Besides, some factors on the flocculation properties have been investigated systematically. At the laboratory scale, the effects of pH, temperature and original turbidity of untreated raw water on the dosage and flocculation performance have been studied, respectively. Simultaneously, the influences of dosage, sedimentation time and mechanical mixing rate on the flocculation properties have been investigated by orthogonal tests at the pilot scale.

However, all the aforementioned factors are external. It has been reported that the structure factors (inner factors), such as the substitution degree of the functional groups, have more strong influence on the flocculation performance in practice (Bratskaya et al., 2009; Ali and Singh, 2009b; Ghimici et al., 2010; Wang et al., 2008, 2009; Yuan et al., 2010; Zhang et al., 2010). Therefore, a series of CMC-CTA samples with various substitution degrees (DS) of CTA were prepared in this work. The effects of cationic content of the flocculants on the flocculation performance were studied at both laboratory and pilot scale. Furthermore, the flocculation mechanism was discussed in detail from the kinetics studies, zeta potential and turbidity measurements.

1 Materials and methods

1.1 Materials

Chitosan was purchased from Shangdong Aokang Biological Co., Ltd. (China), with the degree of deacetylation of 85.2%, and its viscosity average molecular weight is 83.4×10^4 g/mol, calculated from the intrinsic viscosity (Wang et al., 1991). Monochloroacetic acid from Zibo Lushuo Economic Trade Co., Ltd. (China) and CTA from Wuhan Yuancheng Technology Development Co., Ltd. (China) are both C.P. grade reagents and used without further purification. All other chemicals were purchased from Nanjing Chemical Reagent Co., Ltd. (China).

1.2 Preparation of CMC-CTA

CMC-CTA samples are designed and synthesized by two steps as shown in Fig. 1. A desired amount of chitosan is dispersed in isopropanol and NaOH aqueous solution. After stirring and alkalized for 1 hr at 45°C in water bath, a certain amount of CTA is added into the bottle dropwise for 20 min. The resultant solution is stirred for 10 hr at 60°C. The pH of the mixture is then adjusted to pH 7.0 with HCl aqueous solution. The solid is filtered and rinsed in 90% ethanol to desalt and dewater, then extracted using acetone as solvent in the Soxhlet apparatus for 48 hr, and finally dried fully in a vacuum oven at room temperature. The products are Chito-CTA.

Then, a desired amount of dried Chito-CTA sample is added into a mixture of isopropanol and NaOH aque-

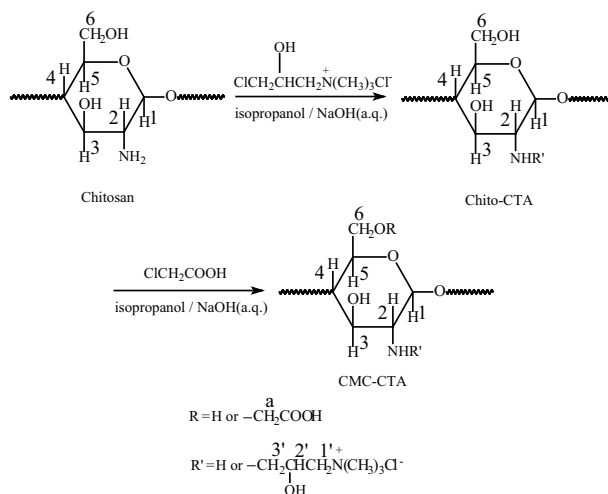


Fig. 1 Reaction route for CMC-CTA.

ous solution to swell and alkalize at 50°C for 1 hr. A certain amount of monochloroacetic acid is dissolved in isopropanol, and added into the reaction mixture dropwise for 30 min and reacted for 4 hr at the same temperature, then stopped by adding 70% ethanol. The pH of the solution is adjusted to pH 7.0 with HCl solution. The solid sample is washed and dried using the same method as mentioned in the first step. The final products of CMC-CTA are prepared.

Four CMC-CTA samples with different DS of CTA are prepared by adjusting the CTA feeding in the first step. The DS of CTA for different CMC-CTA samples and that of carboxymethyl group are both calculated from ^1H NMR spectra. Based on varied CTA contents, the series of CMC-CTA samples are nominated from CMC-CTA1 to CMC-CTA4, respectively. The detailed information about these samples is listed in Table 1.

1.3 Instrument analysis

Fourier Transform Infrared (FT-IR) spectra are recorded using a FT-IR spectrometer (IFS 66/S, Bruker, Germany). The interval of tested wave numbers is $650\text{--}4000\text{ cm}^{-1}$. ^1H nuclear magnetic resonance spectroscopy (^1H NMR) spectra are recorded on a spectrometer (AVANCE DRX-500, Bruker, Germany), operating at 500 MHz, in a mixed solvent containing CF_3COOD and D_2O with a mass ratio of 1:1. Zeta-potential measurement is carried out using a Zetasizer (Nano-Z, Malvern, USA).

1.4 Flocculation experiment

The beaker experiments at the laboratory scale are conducted as follows: Kaolin suspension with original

Table 1 Details of the four CMC-CTA samples.

Sample name	Substitution degree of CTA (%)	Substitution degree of carboxymethyl group (%)	Isoelectric points	Yield (%)
CMC-CTA1	22.0	48.1	5.7	75.3
CMC-CTA2	48.0	47.9	6.3	73.5
CMC-CTA3	52.0	47.5	6.3	72.2
CMC-CTA4	60.0	47.3	6.4	71.0

turbidity of 75 NTU at pH 4.0 and 25°C is used as synthetic water. To dissolve CMC-CTA fully and quickly, the flocculants stock solution is always freshly prepared in 1 wt.% HCl solution before each flocculation test. A known amount of flocculants solution is mixed with synthetic water under magnetic stirring. After 10 min, the kaolin suspension is hold still for a certain time until reaching sedimentation equilibrium. Then, the supernatant is collected for further turbidity and zeta potential measurements. The turbidity is measured by a spectrophotometer (722s, Shanghai Lengguang Tech. Co., Ltd., China) at a wavelength of 550 nm.

Treatment of raw water from Zhenjiang part of Yangtze River (pH: 7.0–7.45; zeta potential: –15 to –20 mV; mean particles diameter: 11 µm; solid concentration: 4‰ to 8‰) at the pilot scale is carried out at Zhenjiang Water Factory in China. The set of equipment has been described in previous works (Zhang et al., 2010; Lu et al., 2011). Its flow chart is shown in Fig. 2, and it includes a raw-water tank (0.66 m in length (L), 0.66 m in width (W), and 0.80 m in height (H)), triple coagulative sedimentation tanks (L × W × H = 1.26 m × 0.42 m × 0.70 m), an inclined-tube settling tank (L × W × H = 2.20 m × 1.20 m × 1.47 m), a sand-filtering column, a clear-water tank, and a backflushing system. The capacity of water treatment, using this equipment, is 1.0 m³/hr, and the mechanical mixing rate in the raw-water tank is 150 r/min. The height of the silicious sand in the sand-filtering column is 76 cm, and the column is backflushed every 24 hr. The soil discharging process in the inclined-tube settling tanks is carried out every 12 hr.

The detailed flocculation experimental parameters are the optimal ones obtained in previous work by orthogonal tests (Yang et al., 2011b) and described as follows: the dosage of the flocculants is 1.1 mg/L; the mechanical mixing rates in triple coagulative sedimentation tank are 150, 100, 50 r/min, respectively; the sedimentation time is 20 min. Turbidity is measured by Turbidity Indicator (ATZ-A22, Wuxi Guangming Instrument Factory, China). The raw water and flocculants were mixed in the raw-water tank, coagulated in the triple coagulative sedimentation tanks, and settled in the inclined-tube settling tank. After filtration in the sand-filtering column, the treated water is stored in the clear-water tank, and turbidity is then measured.

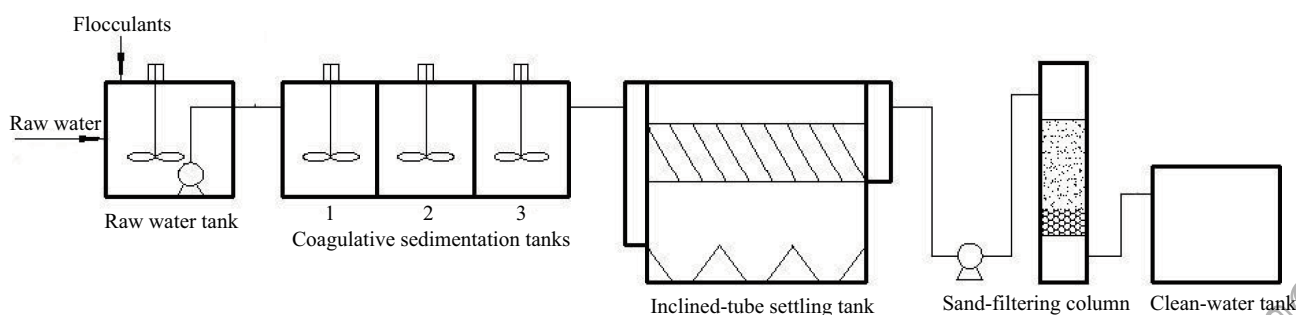


Fig. 2 Flow chart for equipment of flocculation experiment at the pilot scale.

2 Results and discussion

2.1 Characterization of CMC-CTA flocculants

The FT-IR and ¹H NMR spectra of chitosan and the four amphoteric chitosan-based products are shown in Figs. 3 and 4. From their FT-IR spectra, the bands of 3286, 1585, 1151 and 1025 cm⁻¹ in Fig. 3 are attributed to O–H stretch, N–H bend, bridge –O– stretch and primary C–OH stretch in chitosan (Chen and Park, 2003), respectively. New peaks appearing at 1584 cm⁻¹ for COO⁻ groups (Chen and Park, 2003) and 1471 cm⁻¹ for –CH₃ in quaternary ammonium groups (Cai et al., 2007) as shown in Fig. 3 lines b–e demonstrate that carboxymethyl and CTA groups are successfully introduced to chitosan backbone.

¹H NMR spectra also confirm the final structures of the amphoteric flocculants. In addition to the signal of H-2 proton (about 2.95 ppm), H3–6 protons (around 3.25–3.80 ppm) and H-1 proton (about 4.66 ppm) of chitosan (Yuan et al., 2010; Chen and Park, 2003) in Fig. 4 line a, the intense resonances at 2.94 and 3.93 ppm in Fig. 4 lines b–e are attributed to the protons on methyl groups of CTA (Cai et al., 2007) and the carboxymethyl group (Chen and Park, 2003), respectively. And the new peak at about 4.16 ppm is the resonance of H-2' on quaternary ammonium group (Cai et al., 2007). Besides, according to Eqs. (1) and (2), DS of carboxymethyl group and CTA for different CMC-CTA samples are also calculated from ¹H NMR spectra, respectively, as shown in Table 1.

$$DS_{CTA} = \frac{A_{H-2'}}{A_{H-1}} \times 100\% \quad (1)$$

$$DS_{\text{carboxymethyl}} = \frac{A_{H-a}}{A_{H-1}} \times 100\% \quad (2)$$

where, DS_{CTA} (%) and DS_{carboxymethyl} (%) are the DS of CTA and carboxymethyl group, respectively. A_{H-2'}, A_{H-a} and A_{H-1} are the NMR peak areas corresponding to the protons of H-2', H-a and H-1 respectively.

The DS of CTA in varied CMC-CTA samples is various with different CTA feeding, but the content of carboxymethyl groups is kept almost constant.

2.2 Solubility of different flocculants

As mentioned above, the amphoteric chitosan-based flocculants have enhanced solubility in comparison with chitosan and cationic chitosan. Therefore, the solubility of chitosan and different CMC-CTA samples in aqueous solutions with various pH values is tested, and the results

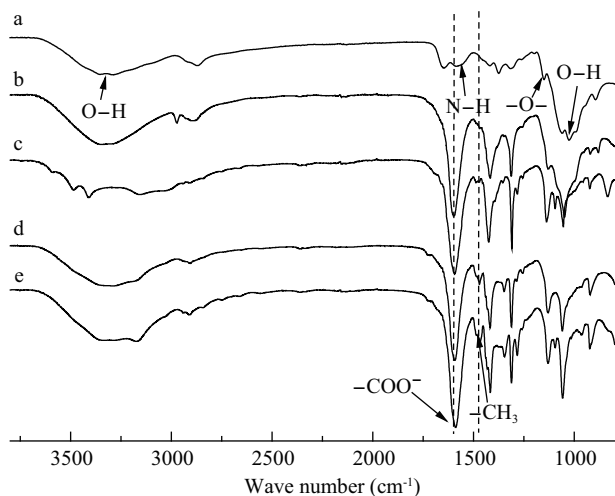


Fig. 3 FT-IR spectra of chitosan (line a), CMC-CTA1 (line b), CMC-CTA2 (line c), CMC-CTA3 (line d), and CMC-CTA4 (line e).

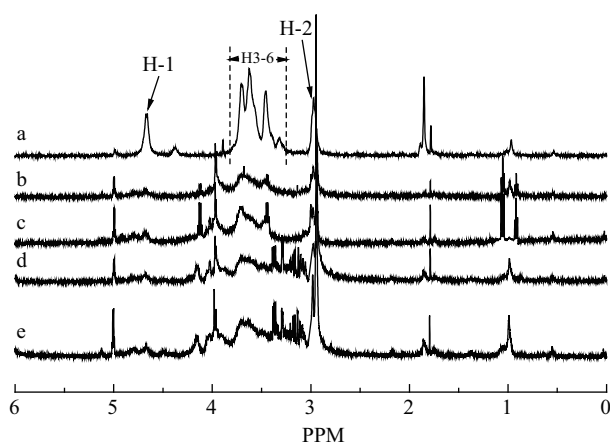


Fig. 4 ^1H NMR spectra of chitosan (line a), CMC-CTA1 (line b), CMC-CTA2 (line c), CMC-CTA3 (line d), and CMC-CTA4 (line e).

are shown in Table 2. As is expected, CMC-CTA samples reveal evidently improved solubility due to the dual characteristics of both anionic and cationic groups, and this phenomenon is fully consistent with our previous report (Yang et al., 2011b).

Furthermore, comparing the four different CMC-CTA samples, it can be found that the solubility becomes better and better with the increase of cationic contents. CMC-CTA4 with the highest DS of CTA is soluble almost at the whole pH range, and only shows partially insoluble near its isoelectric point around pH 6.4. It is ascribed to the fact that the original ordered structure of chitosan has been destroyed largely by the introduced groups.

2.3 Flocculation experiment

2.3.1 Flocculation properties at the laboratory scale

Before the study of the flocculation properties, the zeta potentials of different CMC-CTA aqueous solutions at various pH values are measured and shown in Fig. 5. Since kaolin suspension is used as synthetic water, the zeta potential-pH curve of kaolin suspension is also illustrated in Fig. 5. It is found that kaolin particles are negatively charged over the whole pH range, while various CMC-CTA solutions are all positively charged at lower pH values. Different CMC-CTA samples have different isoelectric points as summarized in Table 1. They are proportional to the CTA content, and CMC-CTA flocculants with higher DS of CTA show higher isoelectric point. In addition, Fig. 5 illustrates that the greatest differences of zeta potential between kaolin suspension and the flocculants solutions appear around pH 4–5. In our previous work (Yang et al., 2011b), it has been found that, in the pH range from 2 to 10, the best flocculation effects of CMC-CTA are always observed at pH 4 at the laboratory scale. The detailed reasons for this phenomenon have been explained as follows: on the one hand, the zeta potential of CMC-CTA is positive at pH 4, and the opposite charges between CMC-CTA and kaolin particles improve the charge neutralization effect. On the other hand, the extensive morphology of the polymeric flocculants due to the intra-chain electrostatic repulsion is also beneficial for flocculation process. Therefore, based on our previous work (Yang et al., 2011b), the following flocculation experiments at the laboratory scale are all carried out at

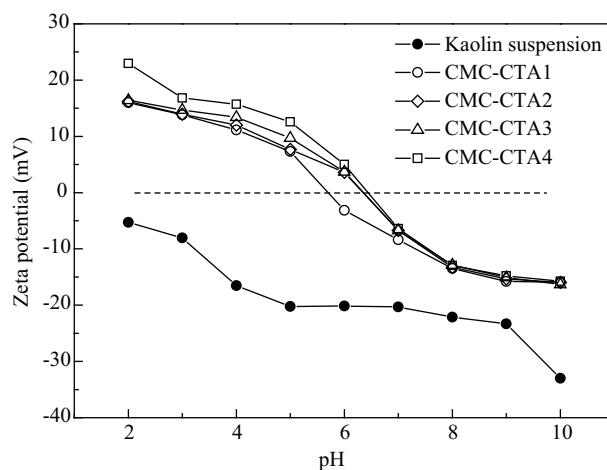


Fig. 5 Zeta potential-pH profiles of kaolin suspension, CMC-CTA1, CMC-CTA2, CMC-CTA3, and CMC-CTA4 solution, respectively.

Table 2 Solubility of different chitosan samples in aqueous solutions with various pH values^a

Sample	Solubility ^b													
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12	pH 13	
Chitosan	+	+	+	-	-	-	-	-	-	-	-	-	-	
CMC-CTA1	+	+	+	±	-	-	±	+	+	+	+	+	+	
CMC-CTA2	+	+	+	+	±	-	±	+	+	+	+	+	+	
CMC-CTA3	+	+	+	+	±	-	±	+	+	+	+	+	+	
CMC-CTA4	+	+	+	+	+	±	±	+	+	+	+	+	+	

^a Each solid sample (100 mg) was dispersed in aqueous solution (20 mL) on the basis of the reported method (Chen and Park, 2003).

^b +: soluble; ±: partially soluble; -: insoluble.

pH 4 to investigate the effect of the substitution degree of CTA.

Figure 6a–d gives the variations of transmittance of the supernatant collected from synthetic water as a function of flocculation time with different dosages of four CMC-CTA samples. It is found that the transmittance of the

supernatant treated by various flocculants increases with increasing flocculation time. This trend indicates that, the flocculation properties can be improved by prolonging the sedimentation time. In addition, a blank experiment without adding any flocculants is performed to evaluate the “natural” sedimentation rate of kaolin suspension,

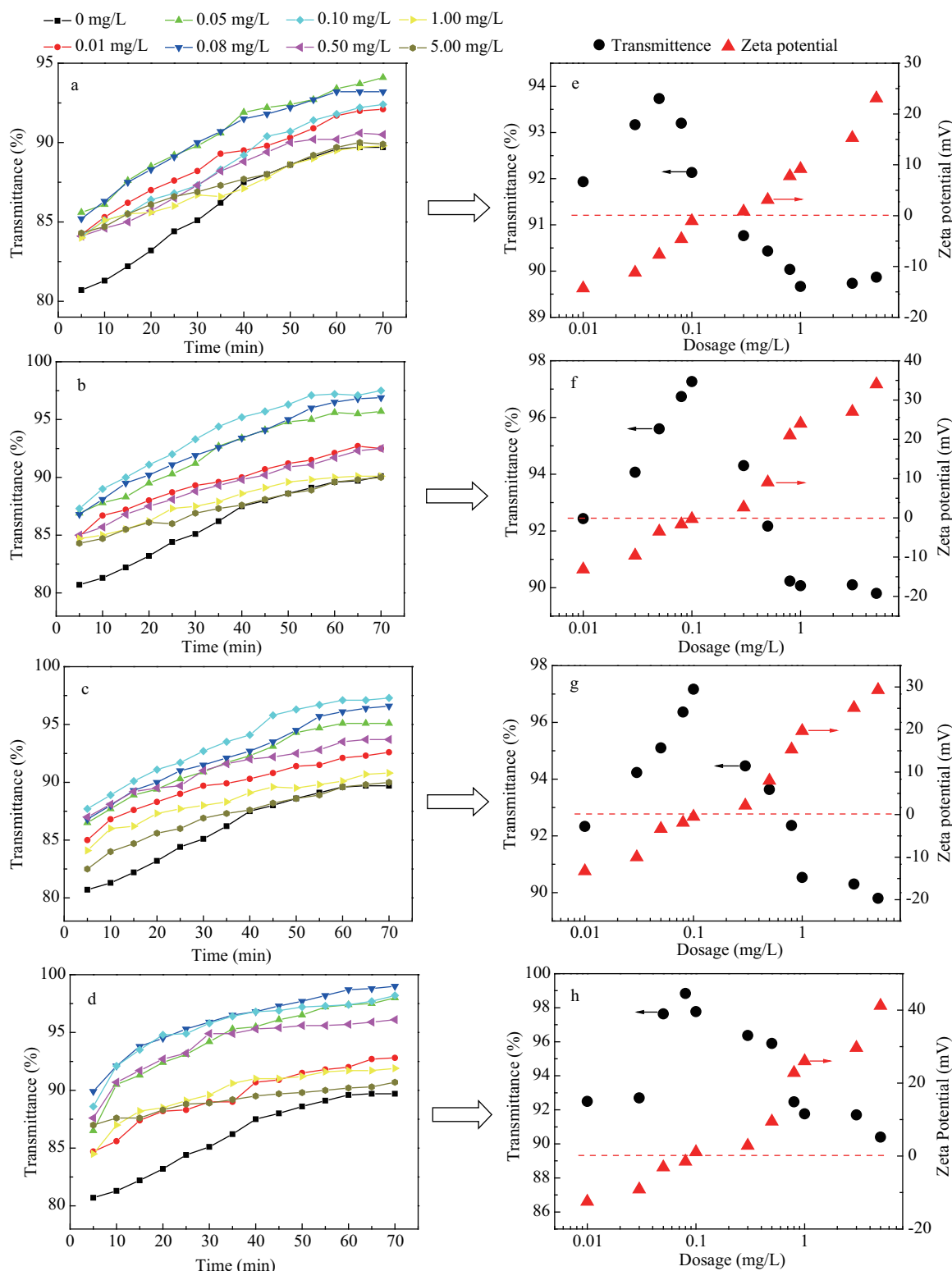


Fig. 6 Flocculation properties of different CMC-CTA samples: Variations of transmittance of the supernatant collected from synthetic water as a function of flocculation time with different dosages of CMC-CTA1 (a), CMC-CTA2 (b), CMC-CTA3 (c), and CMC-CTA4 (d); According to Fig. 6a–d, variations of transmittance and zeta potential of the supernatant collected from synthetic water as a function of dosage of CMC-CTA1 (e), CMC-CTA2 (f), CMC-CTA3 (g), and CMC-CTA4 (h) after reaching flocculation equilibrium.

since kaolin suspension is unstable itself. It is found that the transmittance of the supernatant of the blank sample reaches plateau after near 1 hr, and keeps less than 90% even after 24 hr, which is lower than the values of supernatant treated by flocculants. It illuminates that the polymeric flocculants play an important role in the removal of turbidity from raw water.

Based on Fig. 6a–d, variations of transmittance of the supernatant after reaching sedimentation equilibrium as function of dosage of different flocculants are summarized in Fig. 6e–h. At the same time, the zeta potentials of the supernatant have been also measured and showed in Fig. 6e–h. The variations of transmittance and zeta potential of CMC-CTA2, CMC-CTA3 and CMC-CTA4 show typical trend of flocculation systems controlled by charge neutralization mechanism. With the dosage increase, the transmittance has up-climax-down variation trend, whereas zeta potential increases all the time and is near zero at the optimal dosage. However, as for CMC-CTA1, the negative value of zeta potential at the optimal dosage point may be due to the patching flocculation mechanism. This can be explained as follows: since CMC-CTA1 has the lower cationic content, its polymer chains are not extended enough due to the decreased intra-molecular electrostatic repulsion. Hence, when adsorbing onto kaolin particles, the more coiled chains are easier to form heterogeneous patch-like surface structures (Ghimici and Nichifor, 2010).

Based on Fig. 6e–h and the calculated DS of CTA results as shown in Table 1, the CTA content dependence of the optimal dosage and the corresponding maximum transmittance of the supernatant are summarized in Fig. 7. Although CMC-CTA1 has the lowest optimal dosage due to the patching mechanism, its flocculation performance is the poorest one among the four samples, resulting from the fact that its transmittance of the supernatant is even less than 94%. The poorest flocculation performance can be ascribed to the lowest DS of cationic groups. Therefore, although CMC-CTA1 has the lowest optimal dosage, from the view of cost-effective aspect, it could not be recognized as an efficient flocculant due to its poor flocculation performance. Beside CMC-CTA1, in other three samples, as the DS of CTA increases, lower optimal dosage of flocculants but higher corresponding maximum transmittance of the supernatant is obtained. It is ascribed to the fact that flocculants with higher cationic content have not only higher efficiency in charge neutralization effects, but also more extended structures due to the increased intra-molecular electrostatic repulsion (Flory, 1953; Radeva, 2001), which also enhances the bridging flocculation effects. Hence, it could be concluded from Fig. 7 that, higher cationic content is beneficial for improvement of the flocculation performance of CMC-CTA. This result also agrees well with some reports from other publications (Ghimici et al., 2010; Ghimici and Nichifor, 2010; Pal et al., 2006). In addition, although the optimal dosage of CMC-CTA4 is about twice larger than that of CMC-CTA1, its flocculation performance improves a lot. Hence, CMC-CTA4 can still be recognized as a cost-effective flocculant.

Furthermore, to investigate the effects of CTA content

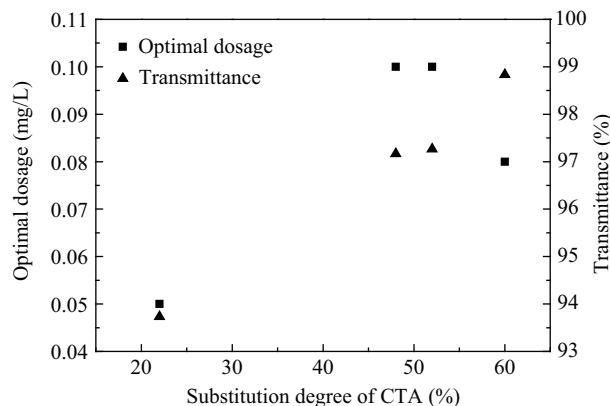


Fig. 7 Optimal dosages of various CMC-CTA samples and their corresponding transmittance of the supernatant as a function of the substitution degree of CTA according to Fig. 6e–h.

further, flocculation kinetics model of particles collisions is employed. It is well known that the order of flocculation process is mostly bimolecular (Chen et al., 2007; Das and Somasundaran, 2004; Deng et al., 1996):

$$\left(\frac{N_0}{N_t}\right)^{1/2} = 1 + \frac{1}{2}kN_0t \quad (3)$$

where, N_0 is the initial number concentration of kaolin particles, N_t is the number concentration of kaolin particles at time t (sec), and k (sec^{-1}) is the rate constant for collisions between the singlets. Moreover, the relationship between transmittance and the number concentration of kaolin particles is:

$$\frac{N_0}{N_t} = \frac{100 - T_0}{100 - T_t} \quad (4)$$

where, T_0 (%) and T_t (%) are the transmittance of the initial water and supernatant at time t (sec), respectively. Therefore, based on original data in Fig. 6a–d, a plot of $[(100-T_0)/(100-T_t)]^{1/2}$ against t will give a straight line with an intercept of 1 for a bimolecular process as described in Fig. 8. kN_0 are also calculated by computer fitting and shown in Table 3.

Since N_0 is a fixed value for the same synthetic water, it is obvious from Table 3 that, the rate constant k at every dosage all increases as the DS of CTA increases. In the case of low cationic content, the interaction between the flocculants and kaolin particles is weak, which results in low k . The enhancement in k with the increase of DS of CTA could be due to the more flocculation sites on the flocculants and higher efficient in charge neutralization effects, which are both beneficial for acceleration of the flocculation process. Hence, the possibilities for molecular collisions between the charge-neutralized kaolin particles become more notable. Besides, based on Fig. 7 and Table 3, k of every CMC-CTA sample always shows the highest value at respective optimal dosage. It is demonstrated that the most efficient collisions will take place at the optimal dosage. Nevertheless, after the optimal dosage, higher dosage of flocculants can also cause a decrease of k . This can be ascribed to the electrostatic repulsive forces between the kaolin particles enwrapped by excessive polymeric flocculants, which hinder their effective collisions.

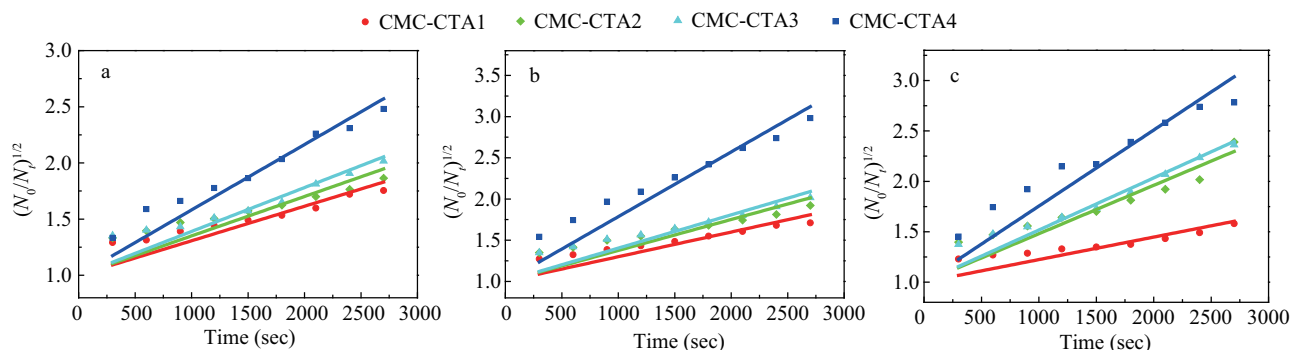


Fig. 8 $(N_0/N_t)^{1/2}$ as a function of setting time at initial concentrations of 0.05 (a), 0.08 (b), and 0.10 mg/L (c) for CMC-CTA1, CMC-CTA2, CMC-CTA3 and CMC-CTA4, respectively, according to Fig. 6a–d. The thin solid lines represent the theoretic simulated curves based on the Eqs. (3) and (4).

Table 3 Simulated results of flocculation kinetics for different CMC-CTA flocculants with various dosages according to Fig. 6a–d

Flocculants dosage	0.05 mg/L		0.08 mg/L		0.10 mg/L	
	kN_0 ($\times 10^{-4}$ sec $^{-1}$)	R^2	kN_0 ($\times 10^{-4}$ sec $^{-1}$)	R^2	kN_0 ($\times 10^{-4}$ sec $^{-1}$)	R^2
CMC-CTA1	6.14	0.995	5.99	0.995	4.47	0.996
CMC-CTA2	7.01	0.993	7.51	0.993	9.60	0.994
CMC-CTA3	7.81	0.995	8.08	0.994	10.3	0.997
CMC-CTA4	11.6	0.996	15.7	0.993	15.1	0.992

Table 4 Flocculation experimental results by different CMC-CTA flocculants at the pilot scale

Sample	Substitution degree of CTA (%)	Water temperature (°C)	Average turbidity (NTU)		
			Before sand filtration	After sand filtration	Raw water
CMC-CTA1	22.0	23.1	8.79	1.32	44.8
CMC-CTA2	48.0	23.3	7.78	0.89	36.8
CMC-CTA3	52.0	22.5	6.68	0.71	40.7
CMC-CTA4	60.0	22.6	5.03	0.47	43.2

2.3.2 Flocculation properties at the pilot scale

For practical applications, besides beaker experiments, the flocculation properties of different flocculants are also studied at the pilot scale.

Table 4 summarizes the flocculation results by the four different CMC-CTA samples. In terms of the calculated results of DS of CTA, it is found from Table 4 that, the average turbidity before and after sand filtration both decreases with the increase of CTA content, which indicates that the flocculation performance becomes better at higher CTA content. This finding is fully consistent with the aforementioned results from beaker experiments at the laboratory scale.

3 Conclusions

Four various CMC-CTA flocculants with different DS of CTA and almost same carboxymethyl content are prepared successfully. All of them exhibit significant advantage in solubility in comparison with chitosan. In addition, the solubility pH region turns larger with the increase of cationic content. Flocculation tests at the laboratory and pilot scale both indicate that, the DS of CTA for CMC-CTA flocculants is a very important factor to the flocculation properties, and higher CTA content will cause better flocculation performance. The flocculants with higher cationic content not only have higher efficiency in charge

neutralization effects, but also show enhanced bridging flocculation effects for more extended structures due to the increased intra-molecular electrostatic repulsion in solutions. Further investigation finds that the flocculation process follows the kinetics model of particles collisions very well ($R^2 > 0.99$), and higher cationic content is beneficial for the increase of the probability for colloids collisions.

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