



Evaluation of chain architectures and charge properties of various starch-based flocculants for flocculation of humic acid from water



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ABSTRACT

Three different starch-based flocculants with various chain architectures and charge properties have been prepared through etherification, graft copolymerization, or their combination. Two of the flocculants (starch-*graft*-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride] and starch-3-chloro-2-hydroxypropyl triethyl ammonium chloride, denoted as STC-g-PDMC and STC-CTA respectively) are cationic, and another one (carboxymethyl starch-*graft*-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride], denoted as CMS-g-PDMC) is amphoteric. Those three flocculants have shown far different flocculation efficiency and floc properties for the removal of humic acid (HA) from water due to their distinct structural features. The effects of pH, flocculant dose, and initial HA concentration have been studied systematically. Accordingly, STC-g-PDMC and CMS-g-PDMC with strongly cationic branch chains have much better flocculation performance than polyaluminum chloride (PAC) and STC-CTA, the latter of which features linear chain architecture and strongly cationic pieces lying on its chain backbone. It indicates that the architecture of cationic branch chains plays an important role in HA flocculation due to their significantly enhanced bridging effects. Moreover, STC-g-PDMC has higher HA removal efficiency and better floc properties than CMS-g-PDMC, suggesting that charge neutralization effects make notable contributions to HA removal and that the additional anionic pieces on CMS-g-PDMC can weaken its flocculation performance. In addition, STC-g-PDMC used as coagulant aid for PAC has also been tried, which observably reduces the optimal dose of the inorganic coagulant.

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1. Introduction

Starch-based flocculants (Bolto and Gregory, 2007) have received much more attentions in the field of water treatment in recent decades due to their significant characteristics of widespread availability, low cost, environmental friendliness, and biodegradability. Although the traditional inorganic and synthetic polymeric flocculants are widely used now, they have always been blamed for the residual metal ions as well as toxic organic monomers (Bolto and Gregory, 2007; Ippolito et al., 2011). However, starch also has many defects in practical use including poor water solubility, low molecular weight, and lack of charge property, causing lower quality and efficiency in water purification. Therefore, many kinds of modified starch flocculants have been manufactured and reported to be able to further improve its flocculation performance (Krentz et al., 2006; Pal et al., 2005; Sen et al., 2009;

Wang et al., 2013) by various chemical modification methods such as esterification, etherification, and graft copolymerization (Lin et al., 2012; Rath and Singh, 1997; Wei et al., 2008).

As is known, the final application performance of a material, including the flocculant, is highly dependent on their molecular structures (Ashby et al., 2013; Ravve, 2013; Wessel, 2004), apart from external environmental parameters such as pH, temperature and dose (Khayet et al., 2011; Li et al., 2004). Therefore, as for flocculants, it is significantly important to build and effectively exploit the structure-activity relationships, as these greatly influence the selection and design of high-performance flocculants in the decontamination of targeted pollutants. However, little work concerning this strategy has been reported in the field of flocculation.

Moreover, far different from small molecular-weight compounds, the structures of polymer materials including starch are quite complicated and contain multiplied levels. Besides the type and chemical composition of the repeating units, the shape and architecture of a macromolecule are also important factors during

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application (Elias, 1984; Ravve, 2013; Sperling, 2005). The structural multiplicity of the polymer materials would result in their varied application performance. As for the research topic related to the development of a novel and high-performance polymeric flocculant, most previous work focused on the design and selection from the perspective of the aforementioned former structural level, types of functional groups and chemical compositions of the flocculants (Lin et al., 2012; Rath and Singh, 1997; Vandamme et al., 2010; Wei et al., 2008; Yuan et al., 2010). However, little work has been done to study the effects of the chain architectures of the polymeric flocculants which have a really great impact on the flocculation performance due to the distinct long-chain feature of macromolecules. Different chain architectures of polymers, including linear, grafting/branching, and star-like forms, would have diverse effects (Elias, 1984; Ravve, 2013; Sperling, 2005). The similar polymers with even the same functional groups but distributed at various positions, the backbone or the side chain of polymers, sometimes have significantly different application performance.

In this work, three starch-based flocculants all containing the strongly cationic quaternary ammonium salt groups but at different positions have been designed and prepared, which bear various chain architectures, i.e. STC-g-PDMC with positive charges on branch chains, STC-CTA with positive charges on starch backbone, and amphoteric CMS-g-PDMC with positive charges on branch chains but a few negative pieces on starch backbone. The effects of chain architectures and charge properties of various starch-based flocculants on flocculation of humic acid (HA) and its floc properties have been investigated in terms of several environmental parameters including pH, dose, and initial HA concentration. HA is a type of water-soluble organic matters in nature, which not only causes yellowish color and undesirable smell of the water (Bratskaya et al., 2004), but is also the main precursor of many disinfection by-products (Richardson et al., 2007). Efficient removal of HA from water remains a thorny issue and has become a hot research topic due to its harm to water environment quality and the poor treatability (Wang and Wang, 2006; Kretzschmar et al., 1997; Lipczynska-Kochany and Kochany, 2008; Yuan and Zydney, 1999). Accordingly, the flocculation performance and mechanisms of aforementioned various starch-based flocculants for HA removal have been studied in detail in terms of their structural characteristics, especially chain architectures and charge properties. The flocculation behavior of polyaluminum chloride (PAC) has been studied together for comparison. Moreover, the combined flocculation using PAC as a coagulant and STC-g-PDMC as a coagulant aid in HA flocculation have also been tried.

2. Materials and methods

2.1. Materials

Starch (weight-average molecular weight of $\sim 1.5 \times 10^5$ g/mol) was purchased from Binzhou Jinhui Corn Development Co., Ltd. Chloroacetic acid (C.P.) was obtained from Zibo Lushuo Economic Trade Co., Ltd. (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC, C.P.) was from Shanghai Bangcheng Biological Technol. Co., Ltd. while (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CTA, C.P.) was purchased from Wuhan Yuancheng Sci. and Technol. Development Co., Ltd. Potassium persulfate (A.R., Shanghai Lingfeng Chemical Reagent Co., Ltd.), the powdered humic acid (sodium salt, Aladdin Industrial Co. Ltd.), and polyaluminum chloride (PAC, $[\text{Al}_2(\text{OH})_n\text{Cl}_{6-n}]_m$, $n = 3.6-5$, $m < 10$, Al_2O_3 content > 28%) were used directly without further purification in this study. All other chemicals were obtained from Nanjing Chemical Reagent Co., Ltd.

2.2. Preparation and characterization of starch-based flocculants

The synthetic routes of STC-g-PDMC, STC-CTA, and CMS-g-PDMC were determined according to the previous literatures (Li et al., 2015; Sen et al., 2009; Wang et al., 2013) and described in detail in Scheme 1. Briefly, STC-g-PDMC was prepared by grafting copolymerization under nitrogen protection and DMC was the grafting monomer while potassium persulfate (KPS) was used as initiator (Wang et al., 2013). STC-CTA was obtained by etherification and CTA was the etherifying agent (Li et al., 2015). A two-step method was used to prepare CMS-g-PDMC by combination of etherification and graft copolymerization. Carboxymethyl starch (CMS) was prepared first and chloroacetic acid was used as the etherifying agent, making water solubility of starch improve markedly. Then PDMC chains were grafted onto CMS backbone in a homogeneous solution using KPS as initiator (Sen et al., 2009; Wang et al., 2013). The three modified starch flocculants were all precipitated in acetone. The obtained solid products were filtered and washed by acetone for three times. Finally, the samples were extracted in a Soxhlet apparatus for 72 h, using acetone as solvent, to remove all the impurities, and then vacuum dried at 45 °C, thereby obtaining the final products. Moreover, the extents of the functional groups in those starch-based flocculants have been estimated by the colloidal titration which was described in detail in our previous work (Zhang et al., 2012). The extents of positive quaternary ammonium salts in STC-g-PDMC, STC-CTA, and CMS-g-PDMC are approximately 2.21, 1.16, and 1.72 mmol/g respectively, while that of carboxymethyl groups in CMS-g-PDMC is about 1.07 mmol/g.

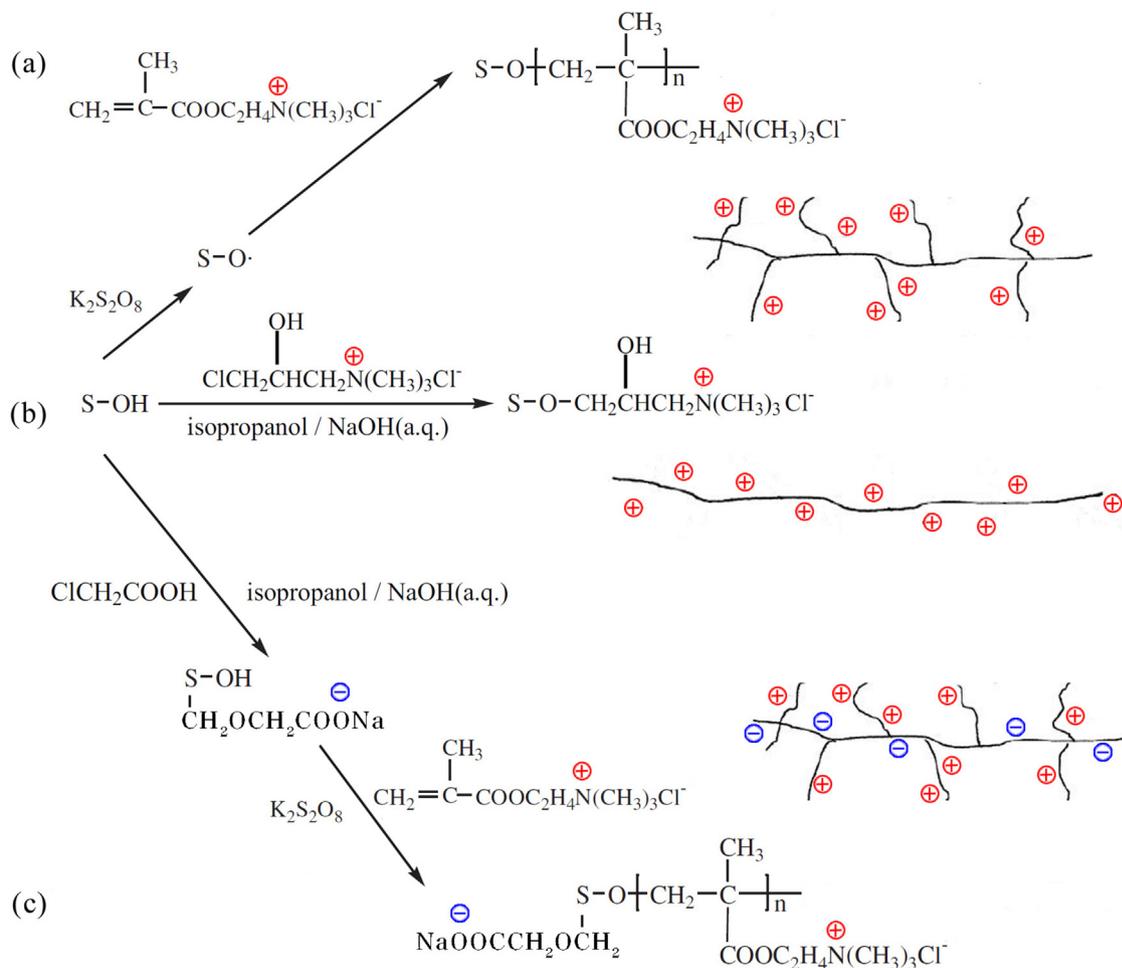
The Fourier transform infrared (FTIR) and ^1H nuclear magnetic resonance (^1H NMR) spectra of the three final products were measured by a Bruker Model IFS 66/S FTIR spectrometer and a Bruker AVANCE Model DRX-500 respectively. The zeta potentials of three flocculants' aqueous solutions with a concentration of 1.0 g/L were recorded by a Malvern Model Nano-Z Zetasizer in a wide pH range from 2.0 to 10.0 adjusted by dilute HCl or NaOH aqueous solutions.

2.3. Flocculation experiments

HA was selected as the target contaminant here and a stock solution was prepared by dissolving 1.0 g of HA into 1.0 L of 1.0×10^{-4} mol/L NaOH solution (Kim, 2015). The actually used HA solutions were diluted to desired concentrations (10, 20, 50, and 100 mg/L respectively), then filtered by glass-fiber filters with a pore size of 0.45 μm .

Jar tests were carried out using 250-mL jars and a six-place programmed paddle mixer model of TA6 (Wuhan Hengling Tech. Co. Ltd.) in water bath at the constant temperature of 25 °C. After the pHs of the HA solutions were adjusted to desired levels by diluted HCl or NaOH aqueous solutions, the designed doses of flocculants were added into the synthetic wastewater. The ionic strength of each solution was kept constant. The detailed flocculation procedure consisted of three steps. (1) The solutions were mixed by a 2-min stir at a high speed of 200 rpm, (2) followed by a slow stir at 50 rpm for 20 min, and (3) finally settled at least 30 min.

After flocculation, the supernatants were taken out for determination of the residual HA concentrations using a UV-1800 spectrometer (Shimadzu Corporation, Japan) in combination with previously prepared calibration curves at the wavelengths of 254 nm. The HA removal percentage was calculated as the following equation:



S-OH: starch

Scheme 1. Synthesis of three starch-based flocculants, (a) STC-g-PDMC, (b) STC-CTA, and (c) CMS-g-PDMC.

$$\text{HA removal percentage}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t are the HA concentrations in aqueous solutions before and after flocculation at equilibrium respectively. All results were measured in triplicate and the final results were the average of the three runs, wherein the relative error was lower than 5.0%.

2.4. Analysis of floc properties

Moreover, the HA floc properties including floc size and two-dimensional fractal dimension (D_2) were also measured by image analysis (IA) (Chakraborti et al., 2000; Liu et al., 2008) in combination with fractal theory (Bushell et al., 2002). Briefly, after sedimentation, the HA flocs were carefully collected from the jars onto a glass sheet with water. A Pentax Model K-m digital camera with a 200-mm lens was used to take photos, from which the characteristic length (l) and the projected area (A) could be calculated with the image analysis software (Imagepro[®] Plus 6.0). Due to the different floc sizes by various flocculants, the proper scales of camera have been adjusted for taking clear pictures. The lengths corresponding to one pixel are 1.74, 1.02, 1.77, 0.98, and 1.05 μm for STC-g-PDMC, STC-CTA, CMS-g-PDMC, PAC, and PAC/STC-g-PDMC

combination respectively. At least three pictures of flocs for each flocculant were taken for obtaining reasonable statistic samples. Here, l is a highly crucial parameter in evaluating the floc size. Then D_2 , describing the compactness of flocs, could be estimated from the exponential relation between l and A as shown in Eq. (2) (Chakraborti et al., 2000; Liu et al., 2008). Larger D_2 indicates denser flocs, which are usually preferred in practical flocculation processes for yielding lower sludge volume as well as reducing the disposal and handling cost.

$$A \propto l^{D_2} \quad (2)$$

3. Results and discussion

3.1. Physicochemical characteristics of three synthetic flocculants

Considering anionic charge features of the HA, flocculants carrying positive charges can be therefore expected to achieve high efficient flocculation of HA due to their significant effects of electrostatic interactions. Accordingly, three different starch-based flocculants with strongly cationic quaternary ammonium salt groups but different chain architectures and charge distributions

have been prepared. The detailed preparation processes were shown in Scheme 1 and briefly described in experiment section. As can be seen from Scheme 1, STC-g-PDMC contains positive charges on branch chains, STC-CTA contains positive charges on starch backbone, and amphoteric CMS-g-PDMC has positive charges on branch chains but a few negative pieces on starch backbone.

For further confirmation of their molecular structures, FTIR and NMR spectra of those three starch-based flocculants were measured and shown in Figs. 1 and 2 respectively. In comparison to the FTIR spectrum of starch in Fig. 1(a), the small characteristic peak in that of STC-CTA (Fig. 1(c)) at 1478 cm^{-1} is ascribed to the methyl of the quaternary ammonium salt groups ($-\text{N}(\text{CH}_3)_3^+$) on CTA (Li et al., 2015), which indicates that CTA was introduced onto the starch backbone successfully (Li et al., 2015). The peak at 1720 cm^{-1} observed in both Fig. 1(b) and (d) corresponds to carbonyl ($\text{C}=\text{O}$) group on the PDMC chain, which provides the evidence of grafting in STC-g-PDMC and CMS-g-PDMC (Cai et al., 2015). In addition, a new band at 1595 cm^{-1} in Fig. 1(d) attributes to carboxyl group, demonstrating the successful substitution of chloroacetic acid to the backbone of CMS-g-PDMC (Cai et al., 2015; Li et al., 2015).

As for ^1H NMR spectra, besides those characteristic peaks of starch based on Fig. 2(a), the significant signal at 3.20 ppm in Fig. 2(c) refers to the protons on the methyl groups of quaternary ammonium groups in CTA (Chen and Park, 2003), and the new emerging signal at around 3.25 ppm in both Fig. 2(b) and (d) is the characteristic peak of methyl protons on the PDMC chain (Cai et al., 2015). Both the FTIR and ^1H NMR spectra can confirm that the three starch-based flocculants, STC-g-PDMC, STC-CTA, and CMS-g-PDMC, have all been obtained successfully.

Then zeta potentials of various starch-based sample solutions have been measured before flocculation measurement and shown in Fig. 3, since charge properties of ionic flocculants would highly affect their flocculation efficiency. It is found that both STC-g-PDMC and STC-CTA bear positive charges and exhibit the characteristics of strong cationic polyelectrolytes in the whole measured pH range (from 2.0 to 10.0). However, as for CMS-g-PDMC, after carboxymethyl groups were introduced onto starch backbones, the positive charges of CMS-g-PDMC reduce much, which shows the typical characteristics of an amphoteric polyelectrolyte with an isoelectric point at pH approximate 7.6. Furthermore, the ZPs of all samples decrease with increasing pH due to the fact that the concentrations of counterions increase.

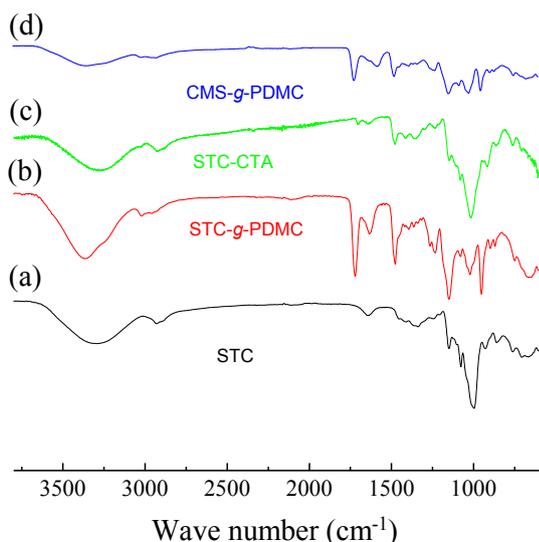


Fig. 1. FTIR spectra of starch (STC), STC-g-PDMC, STC-CTA, and CMS-g-PDMC.

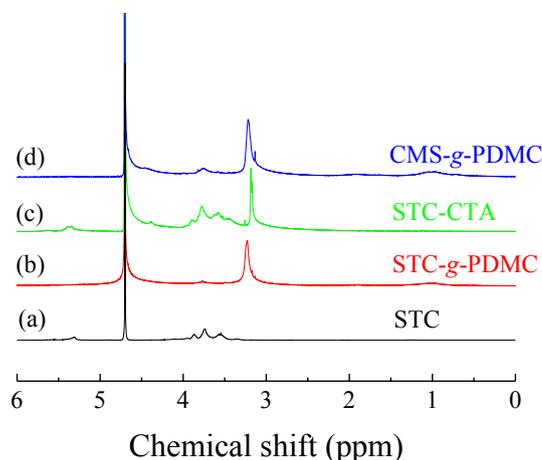


Fig. 2. ^1H NMR spectra of STC, STC-g-PDMC, STC-CTA, and CMS-g-PDMC.

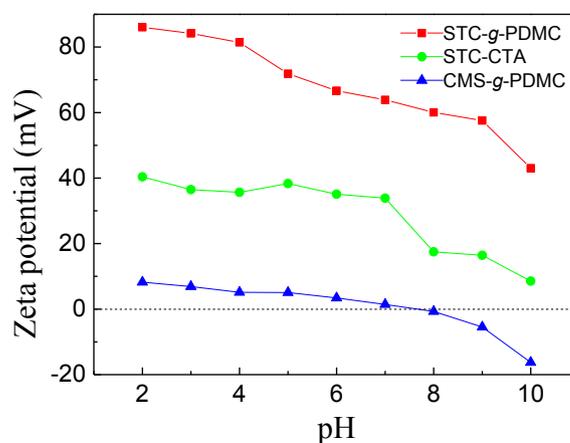


Fig. 3. Zeta – pH profiles of STC-g-PDMC, STC-CTA, and CMS-g-PDMC.

3.2. Flocculation of HA

3.2.1. The effect of pH and dose on flocculating HA

Then the three starch-based flocculants have been employed to flocculate HA from water. As is known, the dose and pH are the two basic external parameters during the flocculation (Chow et al., 1998; Sworska et al., 2000). Therefore, the effects of dose and pH on their flocculation performance including PAC were first compared and illustrated in Fig. 4. In Fig. 4(a–d), the HA removal percentage-dose curves of all measured flocculants at various pH levels display a tendency of rising steadily in the first stage and then decreasing slightly. It is clear that there exists an optimal dose due to charge neutralization (Guibal and Roussy, 2007; Wu et al., 2015; Yang et al., 2014; Yue et al., 2008). However, except for PAC, the restabilization effects at overdose are not notable for three starch-based flocculants, indicating that other flocculation mechanisms may work together in HA removal.

Besides, with descending pH values, the increased HA removal rate of four flocculants can be significantly observed. For further comparison, the pH dependences of optimal dose of various flocculants at HA removal percentages $>90\%$ are summarized in Fig. 4(e) on the basis of Fig. 4(a–d). From Fig. 4(e), it can be seen that the optimal doses of most studied flocculants roughly increased linearly with increasing pH. It may be ascribed to the fact that the positive charges of flocculants decrease (Fig. 3) but the negative charges of HA are more notable with the increase of pH,

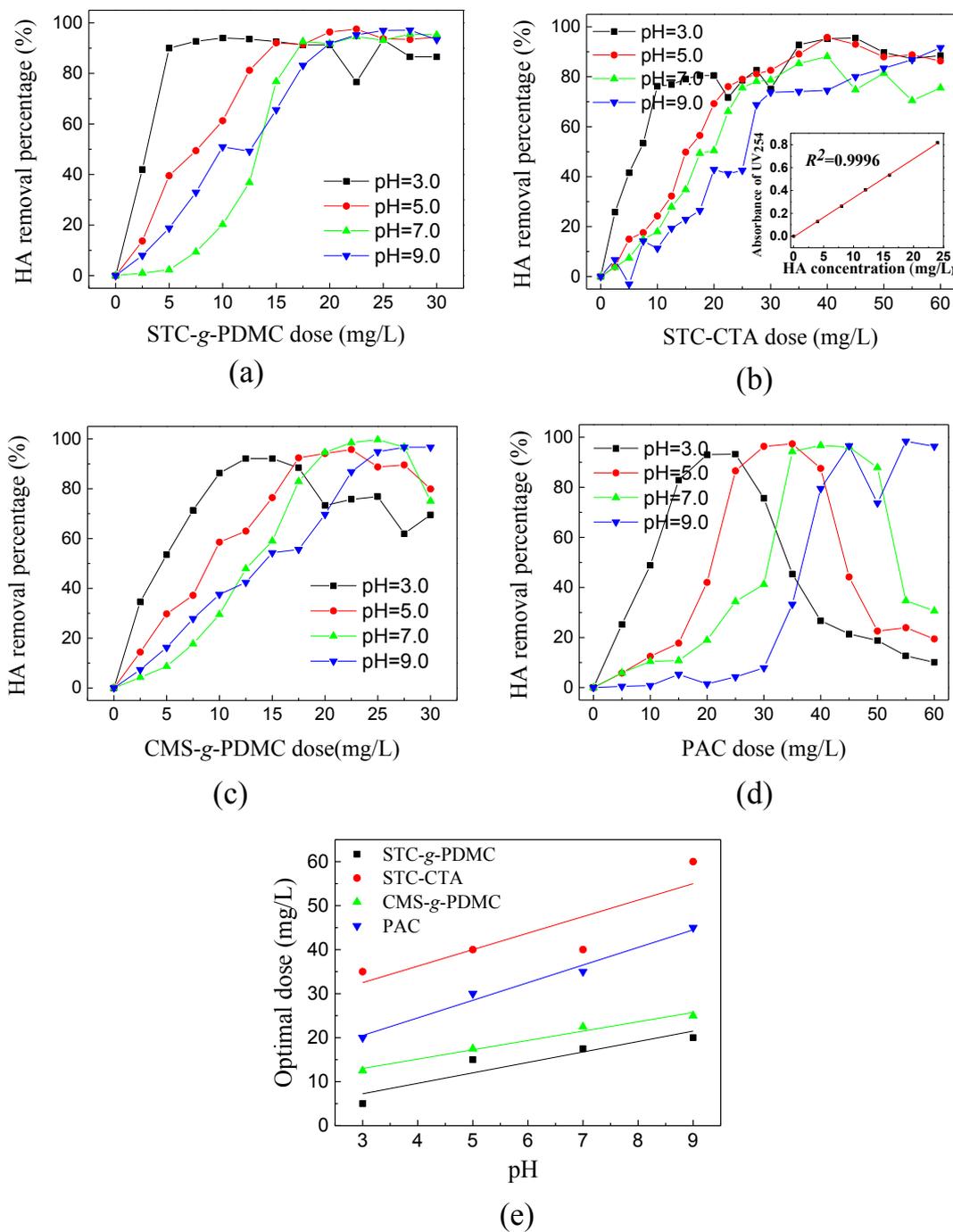


Fig. 4. Flocculation of HA aqueous solution (20 mg/L) with various doses of flocculants at different pHs: (a) STC-g-PDMC, (b) STC-CTA with an insert picture of the calibration curve of the HA, (c) CMS-g-PDMC, (d) PAC, and (e) summary of optimal doses.

which required more flocculants for charge neutralization. In addition, the self-aggregation of HA in water at low pH due to protonation effect might also make some contributions to their improved removal efficiencies. Moreover, according to the optimal doses and HA removal percentage in Fig. 4, different flocculants show evidently different flocculation performance which follows the order of STC-g-PDMC > CMS-g-PDMC > PAC > STC-CTA. STC-g-PDMC possesses the relatively most excellent competence for HA removal while STC-CTA possesses the least among the three studied starch-based flocculants. However, the positive charge properties of STC-CTA are much stronger than those of CMS-g-PDMC

according to Fig. 3. The apparently conflicting results would be discussed in detail in the following section.

3.2.2. The effect of initial HA concentration

Besides pH effects, the varied initial concentrations of the contaminants have essential influences on the final flocculation behavior during a wastewater treatment in reality. Therefore, the effects of initial HA concentrations for three starch-based flocculants and PAC have also been studied at natural condition (pH = 7.0) and shown in Fig. 5.

In Fig. 5(a–d), the HA removal rates of all studied flocculants at

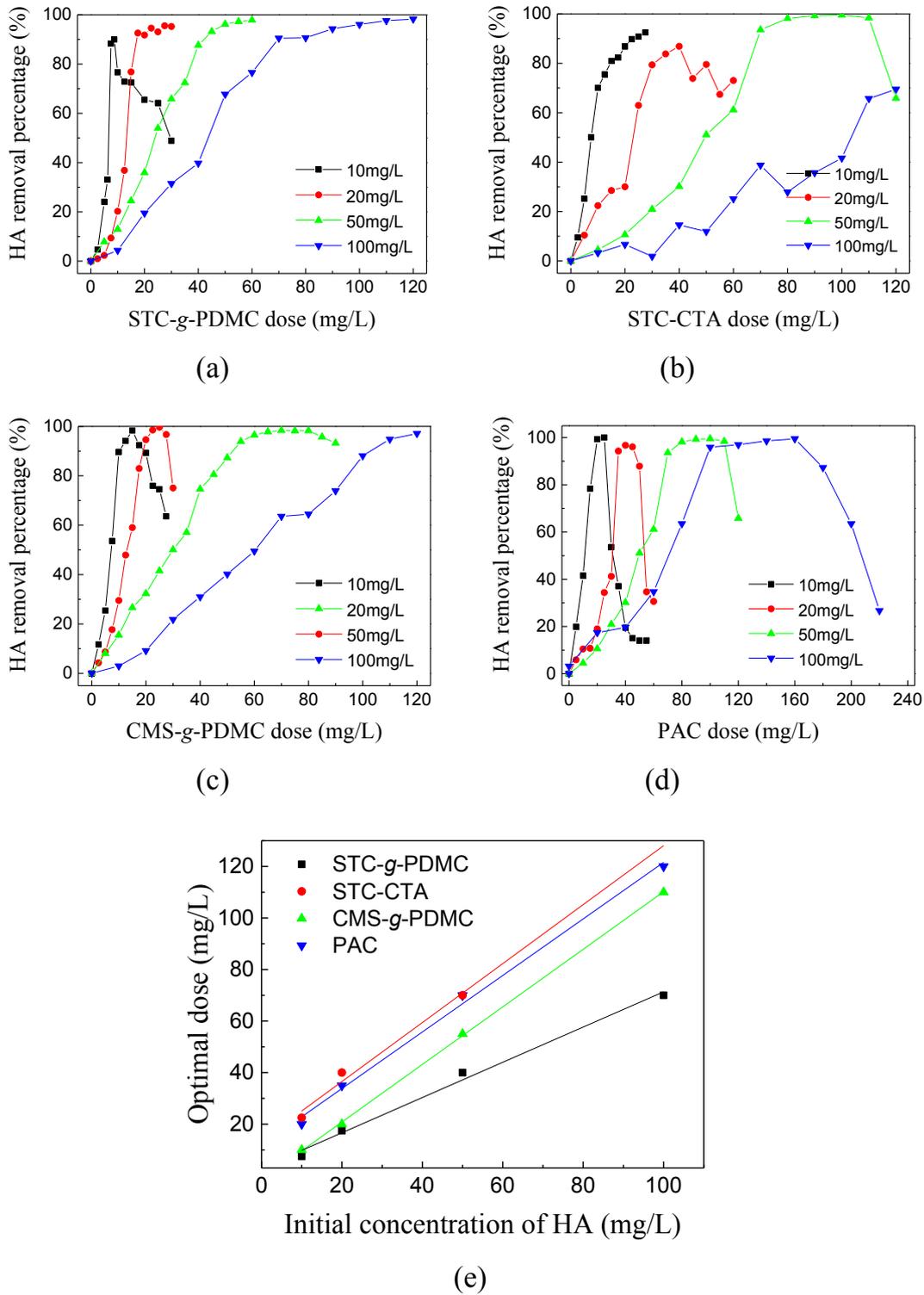


Fig. 5. Flocculation of HA aqueous solutions with different initial concentrations at pH 7.0: (a) STC-g-PDMC, (b) STC-CTA, (c) CMS-g-PDMC, (d) PAC, and (e) summary of optimal doses.

different initial HA concentrations have shown similar trends to those at various pH conditions in Fig. 4(a–d). Fig. 5(e) further summarized the optimal doses of various flocculants. Accordingly, the optimal doses of all studied flocculants linearly increased with increasing initial HA concentrations, which further confirms the effects of charge neutralization (Guibal et al., 2006). This linear relationship can be therefore used to adjust the doses of flocculants

according to the initial HA concentrations in the practical flocculation processes. Moreover, based on Fig. 5, the flocculation performance of different flocculants obeys the similar order to that drawn from their pH dependences as mentioned in previous section, i.e. STC-g-PDMC > CMS-g-PDMC > PAC ≈ STC-CTA. STC-g-PDMC bears much higher efficiency than CMS-g-PDMC and STC-CTA under all experimental conditions which could be easily

explained, since the former possessed the strongest positive charges from Fig. 3. Surprisingly, although CMS-g-PDMC showed the typical feature of an amphoteric material with the lowest positive charges, it still appeared to be more excellent in HA removal than STC-CTA even at pH > 7.6 (Fig. 4), its isoelectric point, at which CMS-g-PDMC was negatively charged. The unexpected results between their flocculation performance and charge properties indicate that charge neutralization effects may not be the main flocculation mechanism in this case.

3.2.3. HA floc properties

Then, the HA floc properties have also been measured to further study and compare the flocculation performance of various starch-based flocculants. In a flocculation process, larger-sized and denser flocs are usually favored for higher sedimentation rate and lower sludge volume, which can efficiently reduce the treatment cost. The characteristic length (l) and D_2 of HA flocs produced by various flocculants at their optimal doses and pH of 7.0 were determined based on image analysis (Fig. 6) and summarized in Table 1.

In Table 1, the flocs sizes follow the order of STC-g-PDMC > CMS-g-PDMC \gg PAC > STC-CTA while D_2 of HA flocs is STC-CTA > STC-g-PDMC > PAC \gg CMS-g-PDMC. Accordingly, STC-g-PDMC and CMS-g-PDMC, both with PDMC cationic branches, formed much larger flocs than other flocculants. Interestingly, STC-CTA bears the smallest floc sizes but the most compacted structure based on its highest D_2 . However CMS-g-PDMC produces the loosest flocs among the all studied flocculants. The unexpected results including not only the HA floc parameters but also aforementioned HA flocculation efficiency are very difficult to be interpreted well using usual explanation such as charge properties. Their intrinsic mechanism may be traced to the distinct structural features of those different starch-based flocculants.

3.3. Combined flocculation

In addition, the cost of those polymeric flocculants is still high, hindering their further practical applications. Therefore, simple, effective, and inexpensive modification techniques need be developed to improve the functionality, application efficiency, and final cost performance of those natural polymer based flocculants. Alternatively, they can be normally used as coagulant aids in combination with inorganic ones to reduce the cost owing to their notable bridging effects. In this section, combined flocculants have been tried in a neutral condition. PAC was used as coagulant and STC-g-PDMC as coagulant aid, since the flocculation performance of the latter was proven to be the best one among the three starch-based flocculants here. The final flocculation behavior of PAC with STC-g-PDMC has been displayed in Fig. 7.

In Fig. 7, after adding a few STC-g-PDMC, the HA removal percentage by PAC increased and the restabilization effects under overdose conditions alleviated observably. Moreover, the optimal doses of PAC linearly decreased with increasing dose of the coagulant aid as seen from the insert image of Fig. 7 due to their synergistic flocculation through bridging and netting effects (Sanghi et al., 2006; Zhang et al., 1999). The dissolved HA was first attracted by the inorganic coagulants resulting in producing small-sized metal/HA complexes (primary flocs); then the addition of the polymeric flocculant was conducive to forming the structure of particle-polymer-particle complexes in which polymeric flocculant functions as a bridge mainly. Obviously, the abundant branch chains on the STC-g-PDMC exerted highly positive effects in this process, further indicating its excellent bridging flocculation effects.

3.4. The flocculation mechanism

As mentioned in Section 3.2, many experimental results of the three starch-based flocculants including their flocculation behaviors and floc properties seem conflicting. They could not be well explained by traditional flocculation mechanisms but by their distinct structural characteristics, since those organic flocculants have different chain architectures and charge properties. Both STC-g-PDMC and CMS-g-PDMC have branch chains with many strongly cationic quaternary ammonium groups while those strongly cationic pieces are distributed on the chain backbone of STC-CTA. From their HA flocculation efficiency illuminated in Figs. 4 and 5, STC-g-PDMC and CMS-g-PDMC both show much more effectiveness in HA removal than STC-CTA under all experimental conditions although similar strongly cationic groups were introduced onto them and the positive charges of CMS-g-PDMC are still much lower than those of STC-CTA. Those experimental facts indicate that the cationic branch chains, which cause enhanced bridging effects, play a more important role in flocculation of water-soluble HA than their charge properties.

Moreover, the branch chains on STC-g-PDMC and CMS-g-PDMC also result in flocs sizes larger than those of STC-CTA (Table 1). However, the rigid linear chain architecture makes STC-CTA, with strongly cationic charges, approach to anionic HA more easily, causing more compacted floc structure and much higher D_2 . As for STC-g-PDMC and CMS-g-PDMC, the closeness of those primary HA flocs to each other has been restricted due to the steric hindrance effects of the PDMC side chains. In consideration of the additional anionic pieces of carboxymethyl groups in CMS-g-PDMC, the internal electrostatic repulsions in primary HA flocs are responsible for its much looser structure. CMS-g-PDMC formed the relatively looser floc structure, although the negatively charged carboxymethyl groups in CMS-g-PDMC may also attract the positively charged graft chains, leading to a relatively compact conformation. It suggests that the negative charges on HA attract the graft chains more strongly than the carboxyls on the starch backbone do.

Shortly, the flocculation mechanisms of three starch-based flocculants can be summarized in Scheme 2. Those cationic polymeric flocculants can play both roles of coagulants and flocculants here. Briefly, (1) during the first stage, the coagulation process, the water-soluble HA would be assembled and adsorbed onto those starch-based flocculants containing strongly cationic groups for efficient charge neutralization effects; and a large number of primary flocs with smaller size are produced; (2) then these flocculant/HA complexes aggregate further to acquire larger-sized flocs, i.e. the flocculation process; here, bridging effect makes main contributions and determines the floc growth. Because of the water-solubility of HA, the second step is the critical one for the performance and bridging effect (Bolto, 1995; Mishra and Bajpai, 2005; Yu and Somasundaran, 1996) plays a preponderant role in flocculating HA for those three starch-based flocculants. As for the combined flocculation by PAC and STC-g-PDMC, the addition of STC-g-PDMC after PAC not only benefits electrostatic attractions to HA in the first stage, but also promotes the aggregation and growth of flocs due to bridging effects in the second stage, both of which result in improved flocculation performance and evident reduction of PAC dose.

4. Conclusions

The HA flocculation behaviors and its floc properties using three starch-based flocculants with different chain architectures and charge properties have been systematically investigated. Those

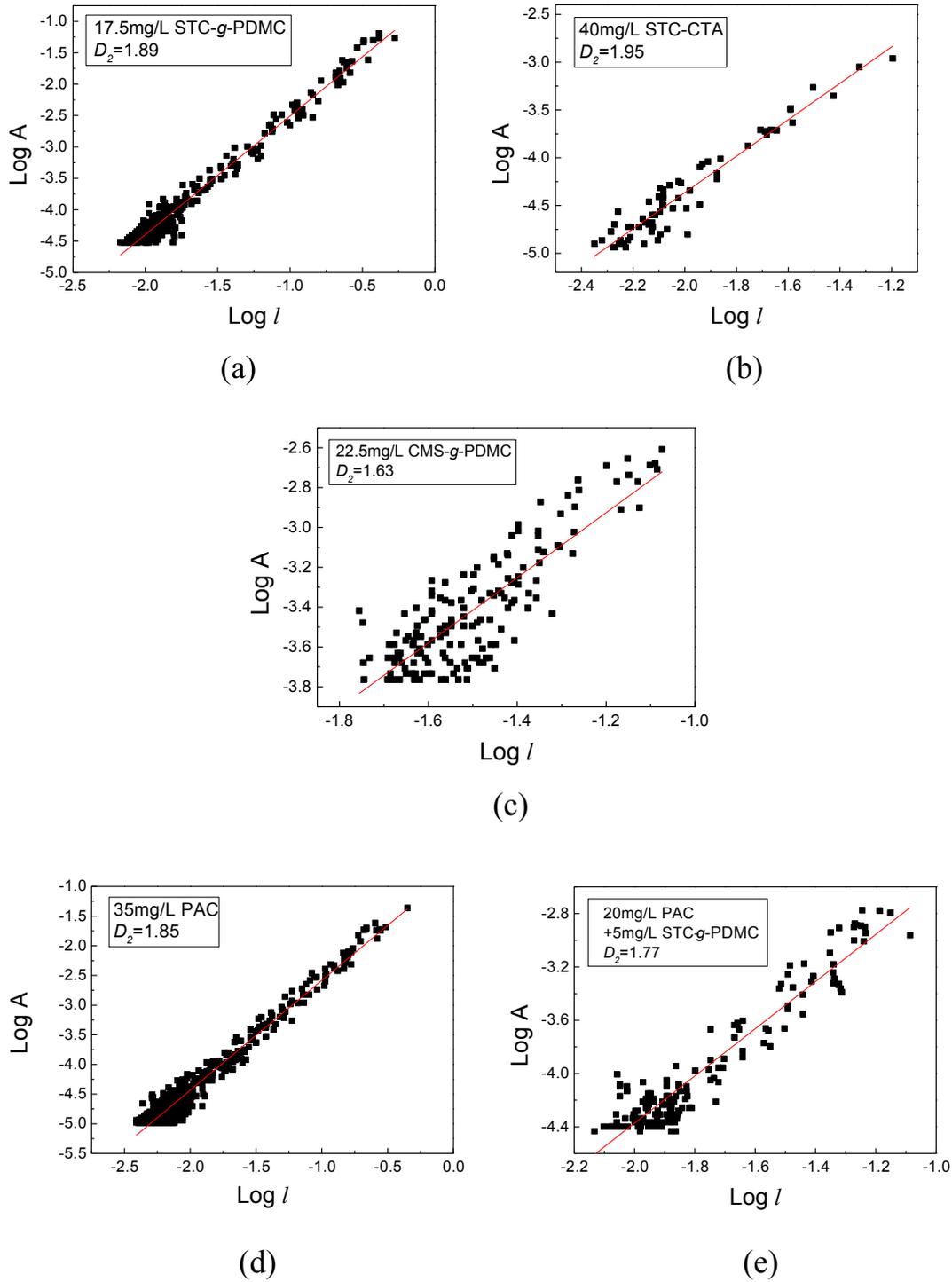


Fig. 6. Image analysis of flocs formed by various flocculants at their optimal doses and pH 7.0.

Table 1
Summary of HA flocculation performance by various flocculants at pH 7.0.

Flocculants	STC-g-PDMC	STC-CTA	CMS-g-PDMC	PAC	Combined flocculants ^a
Optimal dose ^b (mg/L)	17.5	40.0	22.5	35.0	20 mg/L PAC and 5 mg/L STC-g-PDMC
$l_{average}$ (μm)	44.63	12.03	34.11	18.15	20.57
D_2	1.89	1.95	1.63	1.85	1.77
R^2	0.9746	0.9212	0.7043	0.9571	0.9040

^a Combined flocculants contain PAC as coagulant and STC-g-PDMC as coagulant aid.

^b The optimal doses correspond to ones at which 90% of HA removal efficiency can be obtained.

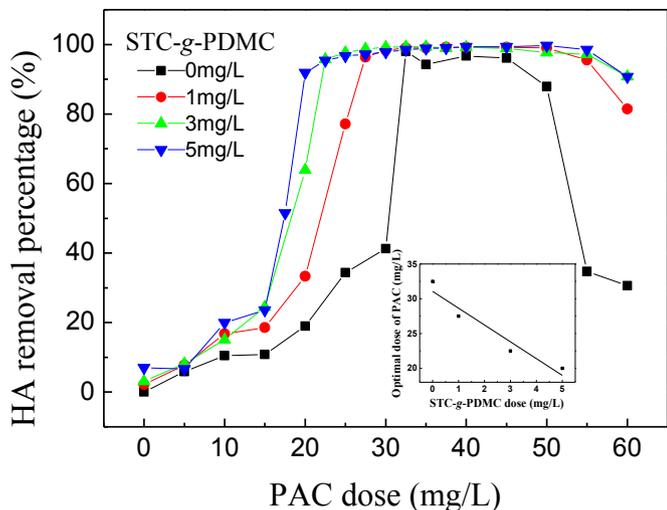
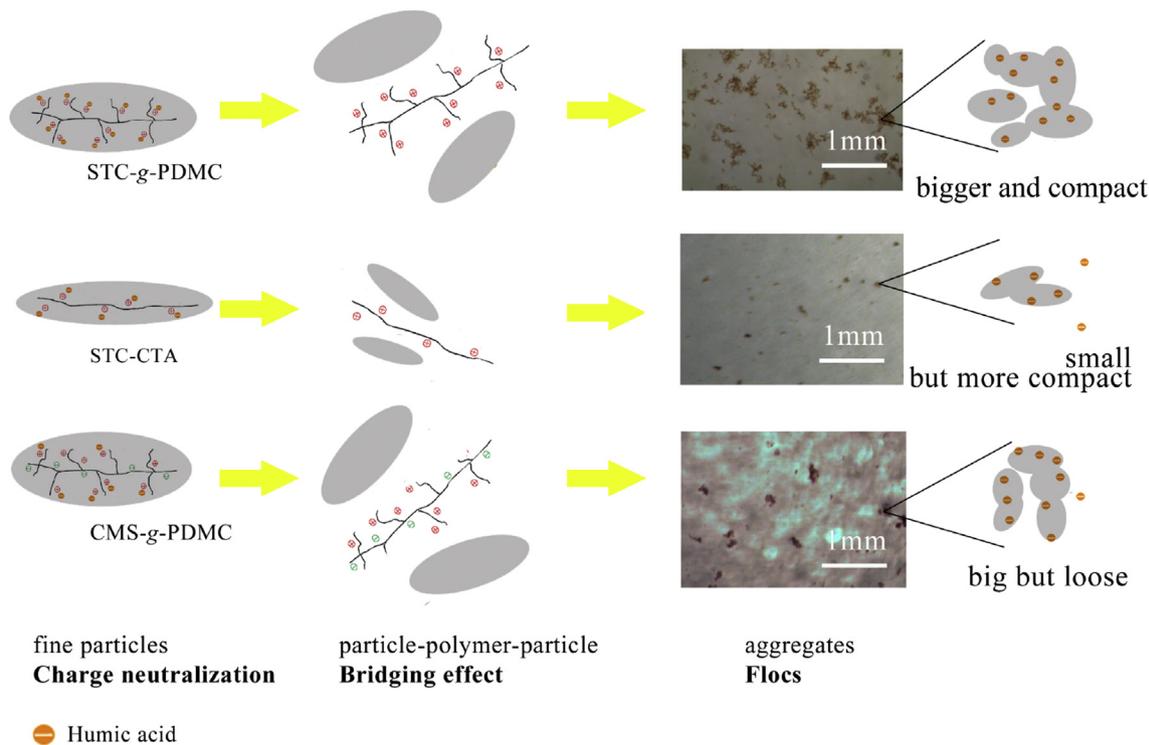


Fig. 7. Flocculation performance of combined flocculants at pH 7.0, PAC as coagulant and STC-g-PDMC as coagulant aid. The inset is the optimal dose of PAC with the dose of STC-g-PDMC.

chain architectures of those three starch-based flocculants. The branch structures of STC-g-PDMC and CMS-g-PDMC result in enhancement of bridging effects, which brings significant benefits to the subsequent floc growth and effective HA removal. However, those grafted chain would also cause the floc structures to be slightly loose due to the steric hindrance effects. In conclusion, bridging effects play a more important role than charge neutralization in the HA flocculation under the experimental conditions in this paper.

Moreover, the flocculation method is popularly employed for removal of both insoluble suspended colloids and dissolved matters like HA. The latter ones are obviously more difficult to flocculate. From this work, the architecture of branch chain for polymeric flocculants brings significant benefits to the removal of water-soluble HA. The result obtained is of importance in guiding the design and selection of a suitable polymeric flocculant in treating target wastewater. Of course, it still needs further experimental evidences to confirm if the flocculants with branch structure are also efficient in flocculation of other dissolved contaminants such as water-soluble dyes, proteins, and polysaccharides in water for more complete and systematic research.



Scheme 2. Flocculation mechanism of three starch-based flocculants for HA removal.

starch-based flocculants had much higher HA removal efficiency in acidic conditions and their optimal doses decrease linearly with decreased initial HA concentrations. Charge neutralization mechanism is responsible for those results in common.

In further comparison, the comprehensive flocculation efficiency, including HA removal percentages, optimal doses, and floc sizes, follows the order of STC-g-PDMC > CMS-g-PDMC >> STC-CTA; while STC-CTA produced the most compacted flocs but CMS-g-PDMC produced the loosest. All of those experimental results are self-consistent and could be well explained in terms of the distinct

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