Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.24852

174 (2020) 171–177
January

Synthesis of an amphoteric chitosan-based flocculant and its flocculation performance in the treatment of dissolved organic matter from drinking water

Xiaomin Tang[a,b,*], Ting Huang[b], Shixin Zhang[c], Jie Zheng[b], Huaili Zheng[c]

[a]*School of Urban Construction and Environmental Engineering, Chongqing University, Chongqing 400045, China, Tel./Fax: +86 02388326467; email: txmno1@126.com (X.M. Tang)*
[b]*Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China*
[c]*Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing 400045, China*

Received 30 April 2019; Accepted 1 September 2019

ABSTRACT

The safety of drinking water arouses wide concern in countries. Dissolved organic matter (DOM) as a precursor of disinfection by-products is the potential threat to human health. An amphoteric chitosan-based flocculant, CS-g-P(AM-AMPS), was synthesized via graft copolymerization to improve DOM treatment in this study. Acrylamide as a trigger and bridge conduced to grafting sulfonate groups originating from 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) onto molecular chains of CS. Initiator dosage, reaction temperature and reaction time influenced the generation of free radicals and further impacted the characteristics and performance of CS-g-P(AM-AMPS). CS-g-P(AM-AMPS) possessing anionic sulfonate groups and cationic amido groups strengthened bridging and adsorption in drinking water treatment, enhanced the removal rate of DOM and the settling efficiency of flocs and weakened the inhibition of natural organic matter to coagulation. DOM was partly removed via co-settling with colloid particles and being trapped by flocs as well.

Keywords: Amphoteric flocculant; Chitosan-based flocculant; Flocculation; Drinking water treatment; Dissolved organic matter

1. Introduction

Drinking water quality is of importance to human health. Some pollutants, like colloid particles, are easily removed from water by the traditional technologies of drinking water treatment, but dissolved organic matter (DOM) is often hard to be completely treated [1–3]. The untreated DOM as a precursor of disinfection by-products has been paid close attention in recent years [4–6]. Coagulation is widely used in drinking water treatment for its low cost in the application and high treatment efficiency [7]. However, coagulation performs not well in the removal of dissolved pollutants, like heavy metal [7] and DOM [8], which increases the load of sand filters that is a plant following coagulation plant in drinking water treatment. It is a challenge to improve the performance of coagulation in DOM treatment.

Flocculant is one of the most important factors in coagulation. The interaction among inorganic flocculants and natural organic matter (NOM) is usually weak [8], but the modified organic flocculants containing multiple functional groups might react with NOM and contribute to its removal from water. Amphoteric organic flocculants may perform better than cationic flocculants, anionic flocculants, and non-ionic flocculants since cationic groups and anionic groups are both discovered in NOM. Besides, the biodegradable natural organic flocculants, such as chitosan (CS), starch and cellulose, are quite suitable to be the safe agent in drinking water treatment [9,10]. The natural organic flocculants should be

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[*] Corresponding author.

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modified via introducing functional groups and lengthening their molecular chains to enhance their treatment efficiencies, their solubility in water and heat stability.

In this study, an amphoteric chitosan-based flocculant, CS-g-P(AM-AMPS), was synthesized via graft copolymerization of CS, acrylamide (AM) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). The main factors in synthesis, the ratio of AM to AMPS, initiator dosage, reaction temperature and reaction time, were investigated to analyze their effects on characteristics of CS-g-P(AM-AMPS). The self-prepared amphoteric flocculant was applied in the treatment of simulated drinking water containing colloid particles, NOM and DOM. It was emphasized to study the removal efficiency of NOM and discuss the main coagulation-flocculation mechanisms.

2. Materials and methods

2.1. Materials and characteristics of drinking water

All chemical reagents used in the study were analytical grade chemicals. Deionized water was used to make all the solutions of reagents. The simulated drinking water was prepared via mixing kaolin powder (Aladdin Biochemical Technology Co. Ltd., China) with deionized water containing fulvic acid and making them dissolving or uniformly dispersing in water. The sizes of kaolin powder were about 5 μm, and the other characteristics of the simulated drinking water are shown in Table 1.

2.2. Synthesis of a CS-g-P(AM-AMPS)

Chitosan (Sinopharm Chemical Reagent Co. Ltd., China), AM (Chengdu Cologne Chemical Co. Ltd., China) and AMPS (Aladdin Biochemical Technology Co. Ltd., China) were successively dissolved in deionized water with rapid stirring. And the initiator, 0.1 mol L^{-1} ceric ammonium nitrate (Aladdin Biochemical Technology Co. Ltd., China), was added into the reactor after oxygen was driven out by nitrogen. The sealed reactor was heated in a water bath for hours and aged at room temperature for 12 h. A CS-g-P(AM-AMPS) containing anionic sulfonate groups and cationic amido groups, was purified by acetone and ethyl alcohol. The solid powder of CS-g-P(AM-AMPS) was obtained in an LGJ-10 vacuum freeze drier (Four-ring Science Instrument Plant Beijing Co. Ltd., China).

2.3. Characteristics of the CS-g-P(AM-AMPS)

Molecular weight and intrinsic viscosity are important parameters for flocculants, which significantly influence the performance of flocculants in water treatment. Intrinsic viscosity was detected via Ubbelohde viscometer, and molecular weight was calculated [11,12]. The grafting parameters, percent grafting (%G) and percent grafting efficiency (%GE), were measured and calculated according to reference and the following equations [13]:

$$\%G = \frac{\left(A_1 - A_2\right)}{A_2} \times 100\% \tag{1}$$

$$\%\text{GE} = \frac{\left(A_1 - A_2\right)}{A_3} \times 100\% \tag{2}$$

where A_1, A_2, and A_3 are the weight of purified CS-g-P (AM-AMPS), the weight of CS and weight of monomers, respectively.

2.4. Jar test procedure

The simulated drinking water containing colloid particles, NOM and DOM was treated by compound flocculants, polyaluminium chloride (PAC) and CS-g-P(AM-AMPS), on a six-paddle gang stirrer (Wuhan Meiyu Instrument Co. Ltd., China). It was operated under the fast stirring of 300 rpm for 2 min and the slow stirring of 40 rpm for 10 min. PAC was firstly added into the simulated drinking water at the beginning of fast stirring, and CS-g-P(AM-AMPS) was dosed after the fast stirring of 1 min. The flocs formed during coagulation-flocculation were settled for 30 min. The turbidity of supernatant was measured by a 2100AN turbidity meter (HACH, USA). The removal rate of turbidity is calculated by the following equation:

$$\text{Removal rate of turbidity} = \frac{\left(T_1 - T_2\right)}{T_1} \tag{3}$$

where T_1 and T_2 are turbidity values of the original drinking water and supernatant, respectively. The absorbance of NOM was measured by a UV-1900 UV/VIS spectrophotometer (SHIMADZU, Japan) at 254 nm, and the absorbance of DOM was measured at 254 nm after the solution was filtered by 0.45 μm membrane filter. The removal rates of NOM and DOM are calculated by the following equations:

$$\text{Removal rate of NOM} = \frac{\left(N_1 - N_2\right)}{N_1} \tag{4}$$

where N_1 and N_2 are absorbances of NOM in the raw drinking water and supernatant after treatment, respectively.

$$\text{Removal rate of DOM} = \frac{\left(D_1 - D_2\right)}{D_1} \tag{5}$$

where D_1 and D_2 are absorbances of DOM in the raw drinking water and supernatant after treatment, respectively.

Zeta potential was measured by a Nano-ZS90 zeta potential analyzer (Malvern Instruments Ltd., UK). As a comparison, PAC and compound flocculants, PAC + polyacrylamide (PAM), were separately operated at the same condition in the treatment of simulated drinking water.

3. Results and discussion

3.1. Key factors in synthesis of the CS-g-P(AM-AMPS)

3.1.1. Effect of the ratio of AM to AMPS

AM plays a link role in grafting AMPS onto CS. Graft copolymerization of AMPS and CS rarely occurs without

AM, and the molecular weight and grafting rate of copolymers are low when AM is few. AMPS tends to self-polymerize and homopolymerize with AM in the process, and the copolymers are hardly dissolved in solution. The undissolved CS-g-P(AM-AMPS) is not able to apply in water treatment. The sufficient AM triggers the yield of free radicals originating from CS, which improves graft copolymerization. The obvious graft copolymerization occurs at the ratio of AM to AMPS of 2:1. The molecular weight of copolymers reaches to the highest when their ratio is 4.6:1. The hydrophilic sulfonate groups and amido groups in AMPS and AM enhance the solubility of CS-g-P(AM-AMPS). However, the high ratio of AM to AMPS decreases the introduction of anionic sulfonate groups.

3.1.2. Effect of initiator dosage

Initiator dosage will influence the generation of free radicals in the grafting copolymerization and further impact on the molecular weight, intrinsic viscosity and grafting rate of CS-g-P(AM-AMPS) [14]. Its molecular weight is a positive correlation with intrinsic viscosity in most cases, and a similar result is found in grafting rate (Fig. 1). The results indicate that the grafting rate increases with the increase of initiator dosage due to the sufficient free radicals generated by the initiator, enhancing the reaction chance among AMPS, AM and CS (Fig. 1b). However, excessive initiator produces a large number of reactive radicals. It leads to the acceleration of copolymerization reaction and the accumulation of reaction heat, which results in primary radical termination, chain transfer and the break of functional groups of CS-g-P(AM-AMPS) (Fig. 1a) [15]. Therefore, CS-g-P(AM-AMPS) possessing the low molecular weight but rich sulfonate groups is found in the synthesis condition of high initiator dosage (Fig. 1). Few initiators reduce the generation rate of free radical, and molecular chains grow slowly in a copolymerization reaction, which leads to the low molecular weight of CS-g-P(AM-AMPS). Initiator dosage should be in the optimal range.

3.1.3. Effect of reaction temperature

Temperature as another essential factor affects the generation of free radicals as well [16]. The high molecular weight and grafting rate are achieved at a temperature of 35°C in synthesis processes (Fig. 2). It implies that CS-g-P(AM-AMPS) can be produced at room temperature, which possesses the obvious advantage in industrial manufacture. The high temperature enhances the reaction rate, though it breaks the molecular chain of copolymers and increases the chance of disproportionation reaction and termination reaction. The molecular weight of copolymers is always

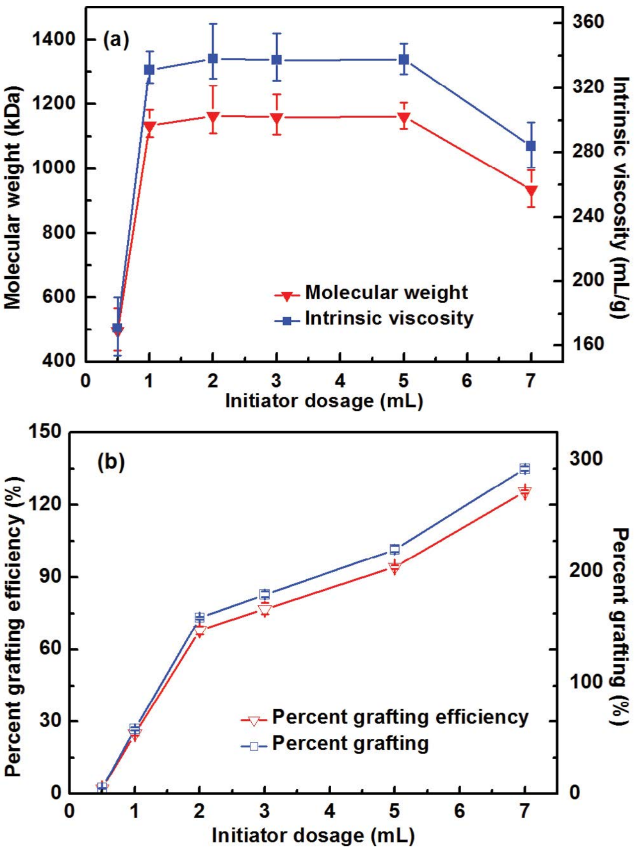

Fig. 1. (a) Molecular weight and intrinsic viscosity and (b) percent grafting efficiency and percent grafting of CS-g-P(AM-AMPS) in different initiator dosages.

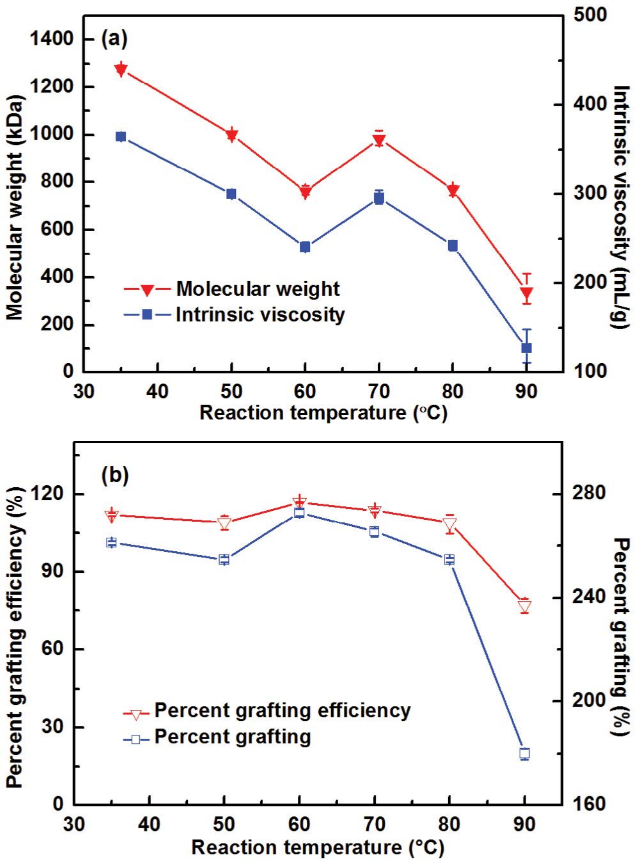

Fig. 2. (a) Molecular weight and intrinsic viscosity and (b) percent grafting efficiency and percent grafting of CS-g-P(AM-AMPS) in different reaction temperatures.

low in the condition of high temperature. The grafting rate markedly decreases when the temperature increases to 90°C (Fig. 2b), and fewer sulfonate groups are successfully grafted onto the molecular chain of CS. Although the temperature of 35°C contributes to the high molecular weight, the generation rate of free radicals is low at low temperatures, and it takes more time in graft copolymerization (Fig. 3).

3.1.4. Effect of reaction time

Reaction time is related to the progress of chain initiation, chain growth and chain termination [14,17]. The short reaction time will result in chain termination in a short time, but the long reaction time does not improve the characteristics of copolymers and even results in the break of molecular chain or functional groups, the aging of copolymers and energy consumption. The molecular weight of CS-g-P (AM-AMPS) significantly increases at the time range of 1 to 2 h. Its molecular weight slowly increases after that, which suggests that chain termination almost occurs. Although the highest molecular weight is obtained at a reaction time of 4.0 h, it is high energy consumption, and the molecular weight does not significantly increase. It is recommended to prepare CS-g-P(AM-AMPS) at 2.0 h.

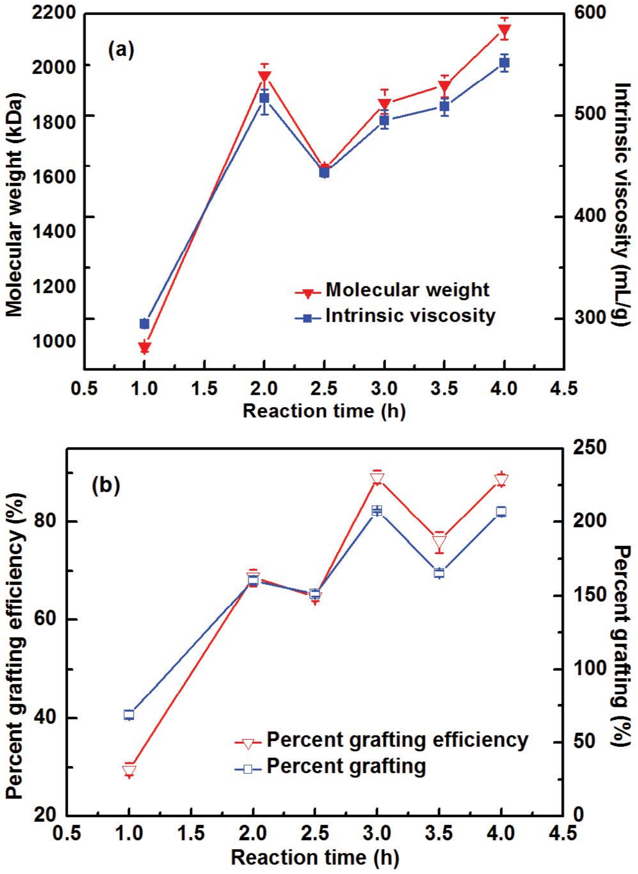

Fig. 3. (a) Molecular weight and intrinsic viscosity and (b) percent grafting efficiency and percent grafting of CS-g-P(AM-AMPS) in different reaction times.

3.2. Performance of the CS-g-P(AM-AMPS) in drinking water treatment

3.2.1. Removal efficiencies of colloid particles, NOM and DOM

Compound flocculants, PAC + CS-g-P(AM-AMPS), performs better than only PAC and compound flocculants of PAC + PAM in drinking water treatment. Although PAC has the acceptable removal rate of colloid particles, its removal rate of organic matter, particularly in DOM, is low (Fig. 4). And a large amount of PAC is added into the water to remove organic matter. It has been reported that a handful of PAC also has excellent performance in the treatment of water containing only colloid particles [18]. It implies that some organic matters can react with PAC, which impedes coagulation. CS-g-P(AM-AMPS) added into the treatment with PAC partly overcomes this hindrance. It increases the removal rates of colloid particles and organic matter. Its treatment efficiencies are higher than the commercial PAM since PAM is nonionic flocculant. The removal rate of awkward DOM is above 60%, which is treated by PAC + CS-g-P(AM-AMPS) since the cationic functional groups and the anion functional groups of CS-g-P(AM-AMPS) react and adsorb with DOM.

3.2.2. Settling efficiency

Settling efficiency is another key factor in coagulation-flocculation. The short settling time reduces the duration of stay and the volume of the sedimentation plant. The large flocs are often related to the high settling rate [19]. The flocs yielded by PAC, PAC + CS-g-P(AM-AMPS) and PAC + PAM have different floc sizes in the treatment (Fig. 5). PAC + CS-g-P(AM-AMPS) forms the largest flocs during coagulation-flocculation, and most flocs settle to the bottom of the container in 5 min. On the contrary, the flocs formed by PAC are small, and they need 30 min to settle to the bottom.

A similar conclusion is discovered in the removal rates of colloid particles and DOM by PAC, PAC + CS-g-P (AM-AMPS) and PAC + PAM with the different settling time (Fig. 6). The flocs generated by PAC are smaller than that formed by the compound flocculants, and more time is required for settlement. Its performance gradually becomes better with the increase of settling time. However, performances of compound flocculants slightly change during the settling time after 5 min, and PAC + CS-g-P(AM-AMPS) has the highest settling efficiency.

3.2.3. Effect of pH on performance

pH influences the chemical and physical properties of pollutants. Their surface charges, for instance, are different at various pH. It also influences the hydrolysis of PAC and its coagulation efficiency [18]. The hydroxyl aluminum in PAC easily transforms into the aluminum hydroxide precipitation of aluminum hydroxide gel at basic conditions, which largely decreases the coagulation efficiency of PAC [18,20]. Furthermore, the deprotonation of functional groups in CS-g-P(AM-AMPS) under basic conditions results in the deterioration of its performance. The results represent that

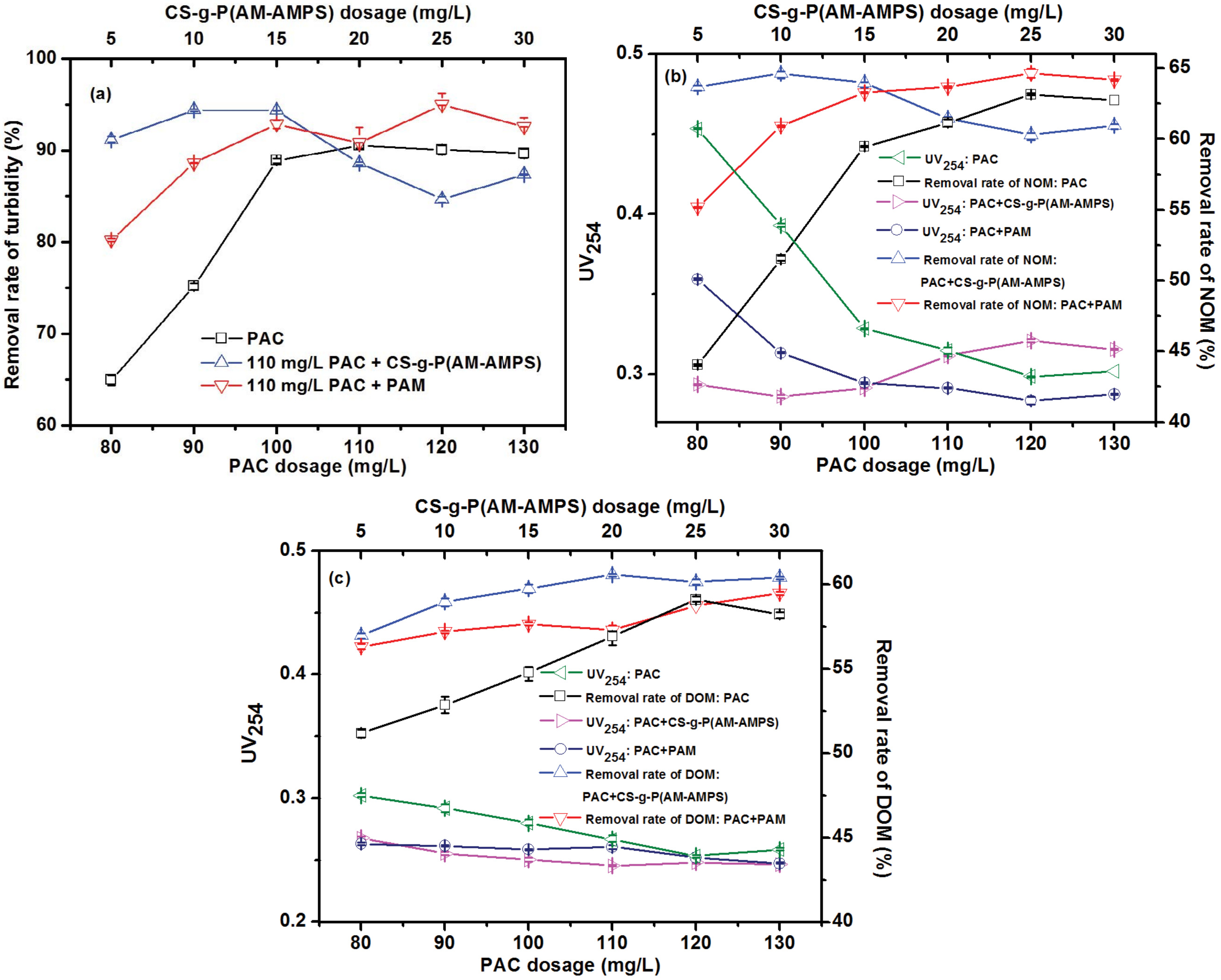

Fig. 4. Removal efficiencies of (a) colloid particles, (b) NOM, and (c) DOM by PAC, compound flocculants of PAC + CS-g-P(AM-AMPS) and compound flocculants of PAC + PAM.

PAC + CS-g-P(AM-AMPS) performs better in weak acid and neutral solution (Fig. 7).

3.3. Coagulation–flocculation mechanisms

The zeta potential of simulated drinking water is negative. The negative charge is mainly found at the surface of colloid particles and NOM (Table 1). Zeta potential increases with the increase of PAC dosage, and PAC plays the dominant role in charge neutralization to treat the drinking water (Fig. 8). It has been reported that the optimal removal rate of colloid particles was obtained when the zeta potential of treated water was near zero [18]. However, the zeta potential is far below zero when PAC achieves the best performance in this study (Figs. 4 and 8). It implies that the untreated NOM/DOM results in the low zeta potential and some NOM/DOM impede coagulation. Charge neutralization is not the only coagulation-flocculation mechanism in the treatment. CS-g-P(AM-AMPS) contains the anionic sulfonate groups and cationic amido groups, and the zeta potential of supernatant does not significantly change with the different dosages of CS-g-P(AM-AMPS). CS-g-P(AM-AMPS) with the various functional groups, anionic groups and cationic groups reacting with functional groups in NOM/DOM through charge attraction and van der Waals force, strengthens bridging and adsorption in pollutants removal, particular in DOM removal, and improves the settling efficiency of flocs (Figs. 4 and 8). DOM is also treated through co-settling with colloid particles and being trapped by flocs.

4. Conclusions

A CS-g-P(AM-AMPS), was prepared via grafting AMPS and AM onto the molecular chain of CS. AM conducted to graft copolymerization as a trigger and bridge since CS rarely reacted with AMPS without AM. Initiator dosage, reaction temperature and reaction time influenced the generation of free radical and further affected the molecular weight, grafting rate and performance of CS-g-P(AM-AMPS). Its optimal molecular weight and grafting rate were achieved through

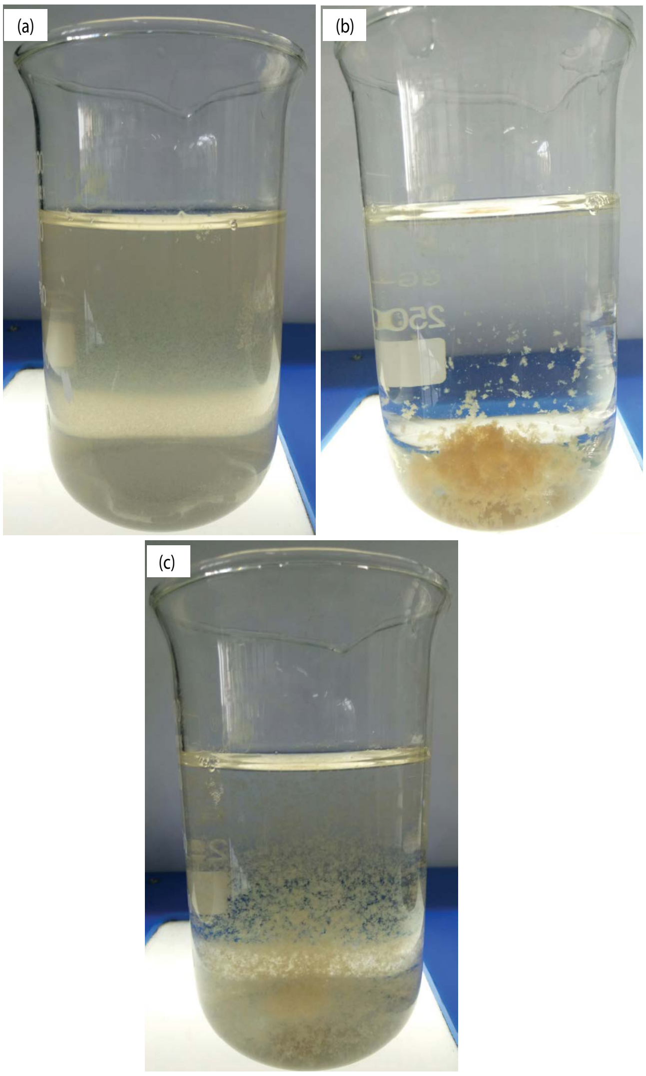

Fig. 5. Flocs formed by (a) PAC, (b) PAC + CS-g-P(AM-AMPS), and (c) PAC + PAM.

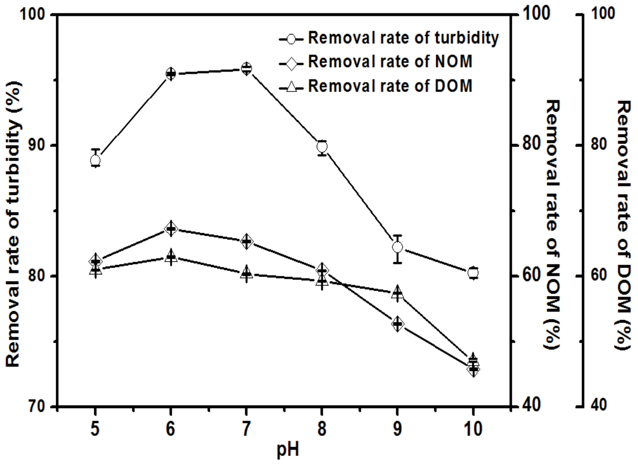

Fig. 7. Effect of pH on performance of PAC + CS-g-P(AM-AMPS) in drinking water treatment.

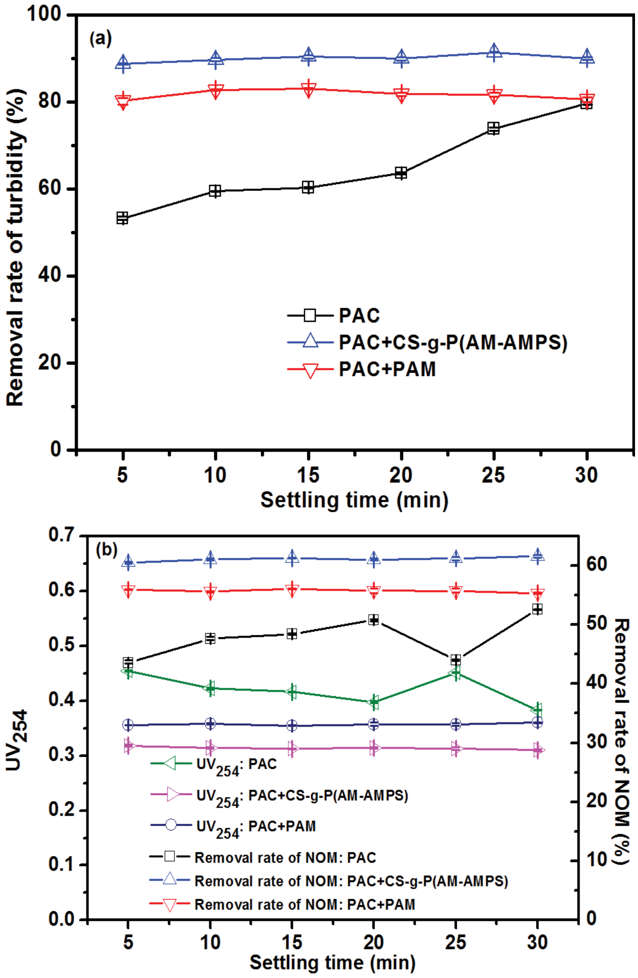

Fig. 6. Settling efficiencies of flocs formed by PAC, PAC + CS-g-P(AM-AMPS) and PAC + PAM.

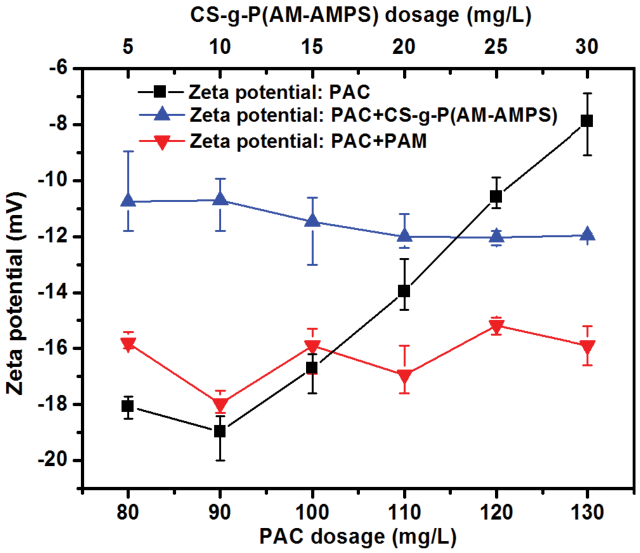

Fig. 8. Zeta potential of water treated by PAC, PAC + CS-g-P(AM-AMPS) and PAC + PAM.

Table 1
Characteristics of simulated drinking water

Name	Parameter value
Turbidity (NTU)	25 ± 0.5
UV_{254} of NOM	0.811 ± 0.003
UV_{254} of DOM	0.619 ± 0.002
pH	7.84 ± 0.10
Zeta potential (mV)	–23.3 ± 0.6

Note: UV_{254} = ultraviolet absorbance at 254 nm

controlling preparation conditions in moderate ranges. The removal rates of colloidal particles, NOM and DOM by PAC were significantly improved via introducing CS-g-P(AM-AMPS) into the treatment. CS-g-P(AM-AMPS) weakened the inhibition of NOM to coagulation and enhanced the settling efficiency of flocs. The flocs formed by PAC + CS-g-P(AM-AMPS) almost settling in 5 min were markedly larger than that formed by only PAC and PAC + PAM. The pH of water influenced the surface charge of pollutants, the hydrolysis of PAC and the deprotonation of functional groups in CS-g-P(AM-AMPS). CS-g-P(AM-AMPS) possessing anionic and cationic functional groups strengthened bridging and adsorption in DOM treatment. DOM was partly removed via co-settling with colloid particles and being trapped by flocs as well.

Acknowledgments

We are grateful for the financial support provided by the National Natural Science Foundation of China (Project No. 51608078), Natural Science Foundation and Advanced Research Project of Chongqing CSTC (Project No. cstc 2016jcyjA0197), China Postdoctoral Science Foundation funded project (Project No. 2017M622970), Project funded by Chongqing Special Postdoctoral Science Foundation (Project No. Xm2017035) and Chongqing Technology and Business University Scientific Research Foundation (Project No. 1756004).

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