

Homogeneous synthesis and characterization of polyacrylamide-grafted cationic cellulose flocculants

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ABSTRACT: In this work, cationic cellulose (CC) with different degrees of substitution (DS) was successfully synthesized by the reaction between cellulose and 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) in a 7 wt % NaOH and 12 wt % urea aqueous solution. The structure of the CC was characterized by using elemental analysis, ¹H-NMR, and FTIR. The DS values of CC ranged between 0.18 and 0.50, which could be obtained by adjusting the reaction temperature, reaction time, and molar ratio of CHPTAC to anhydroglucose unit of cellulose. The cationic cellulose-graft-polyacrylamide flocculant (CC-g-PAM) based on CC and polyacrylamide (PAM) was also synthesized in a homogeneous aqueous solution. The flocculation characteristics of CC and CC-g-PAM were evaluated in a kaolin suspension. The results showed that CC-g-PAM was an effective flocculant for the kaolin suspension under acidic or neutral conditions, and the flocculation efficiency was over 90%, while the CC showed better flocculation performance under alkaline conditions. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43106.

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INTRODUCTION

Flocculation is a process wherein colloids come out of suspension in the form of larger-sized clusters. It is the most efficient and economical method for water purification, and it is widely employed in the purification of drinking water, as well as sewage treatment, storm-water treatment, and treatment of other industrial wastewater streams.

In general, three groups of flocculants can be identified in the literature at the present time: inorganic flocculants such as poly(aluminum chloride),¹ organic synthetic polymer flocculants such as polyacrylamide (PAM)² and poly(ethylene imine),³ and natural organic flocculants such as chitosan,⁴ dextran,⁵ and cellulose.⁶ Inorganic flocculants are cheap but have some drawbacks: they have to be used in large quantities, which results in a lot of sludge, and the metal ion of inorganic flocculants that remains in treated water may have an adverse effect on metal equipment and human health.⁷ Organic synthetic polymeric flocculants are more effective than inorganic flocculants because efficient flocculation occurs at lower dosage (1–6 mg/L compared with 25–100 mg/L for inorganic flocculants).⁸ Furthermore, the properties of organic synthetic polymeric flocculants can be adjusted by controlling the molecular weight and its distribution, chemical structure, nature, and ratio of functional groups on the polymeric backbone.⁸ However, industrial applications of organic synthetic polymeric flocculants may be restricted because of the high cost of the monomers, poor biodegradability, and shear stability.^{7–10} Therefore, an effective and economical flocculant with more sustainable alternatives, such as polysaccharides, is desirable for industrial applications.

Cellulose is one of the most abundant natural polysaccharides on Earth. Therefore, the modification and utilization of cellulose as a flocculant in wastewater is significant. Yan *et al.* used cellulose reacted with 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) in a NaOH/urea aqueous solution to prepare quaternized celluloses.¹¹ Song *et al.* synthesized amphoteric cellulose by etherification of microcrystalline cellulose with CHPTAC and 3-chloro-2-hydroxypropane sulfonic acid sodium.¹² These flocculants are fairly shear stable and biodegradable in contrast with long-chain PAM, but their required dosage is large due to lower efficiencies.⁸

Chemical modification on cellulose has become an important resource for developing advanced flocculants.^{13–15} Among the

various modification methods of natural polysaccharides, graft copolymerization of synthetic polymers, such as polyacrylamide onto cellulose, is one of the most useful methods, and the obtained products essentially combine the advantages of both synthetic and natural polymers. They are biodegradable, non-toxic, and fairly shear stable because of the attachment of flexible synthetic polymers onto the rigid polysaccharide backbone.¹⁶ Several biodegradable polymeric flocculants based on cellulose and its derivatives (like hydroxypropyl methyl cellulose and carboxymethyl cellulose) have been reported as efficient flocculants for the treatment of wastewater.^{16–19} Das *et al.* prepared high-performance flocculant (HPMC-g-PAM) using hydroxypropyl methyl cellulose and PAM raw materials. They found that the HPMC-g-PAM shows better flocculation efficacy than the polysaccharide-based flocculants.¹⁸ Liu *et al.* have prepared bamboo pulp cellulose-graft-polyacrylamide flocculant (BPC-g-PAM) by free-radical graft copolymerization in a NaOH/urea solution, and the flocculation of the BPC-g-PAM was evaluated using the standard kaolin suspension and effluent from a paper mill.¹⁹ The turbidity removal of the BPC-g-PAM reached 98.0% accompanying significant flocculation and sedimentation in the target suspensions.¹⁹ However, PAM is easy to hydrolyze under strong alkaline conditions,²⁰ which has a prominent influence on the flocculation properties of the products. In this paper, microcrystalline cellulose was dissolved in NaOH/urea aqueous solutions, and then the cationic cellulose (CC) was prepared from the CHPTAC and cellulose solutions. Moreover, the flocculant was synthesized based on the CC and PAM in a homogeneous aqueous solution.

EXPERIMENTAL

Materials

The microcrystalline cellulose, a CHPTAC aqueous solution (60 wt %), and PAM (molecular weight, $2\text{--}4 \times 10^6$ D) were purchased from Aladdin Industrial (Shanghai, China). Ammonium persulfate (APS; analytical grade; Sinopharm Chemical Reagent Co., Shanghai, China) was recrystallized from water before use. Kaolin clay (superfine grade with a mean particle size of 11 μm ; Sinopharm Chemical Reagent Co.) was used as received. All other chemicals in this study were analytical grade and used without further purification.

Preparation of CC Solution

The cellulose solution was prepared according to the method described previously.²¹ Briefly, 2 g of microcrystalline cellulose was added to a 49 g 14 wt % NaOH aqueous solution precooled to 0°C with stirring for 1 min. Then, 49 g 24 wt % urea aqueous solution precooled to 0°C was added immediately into it with vigorous stirring for 2 min at room temperature. Within this time, a transparent cellulose solution was obtained, and then a modest centrifugal separation (2500 rpm for 15 min at 10°C) was applied to remove the undissolved part from the cellulose solution before using it further.

In a typical sequential addition procedure, a certain amount of CHPTAC aqueous solution (60 wt %) was added dropwise into the 150 g cellulose solution obtained previously. After all of the CHPTAC (Table I) had been added, the reaction solution was stirred for a certain time at a certain temperature. The product

Table I. DS of CC under Different Reaction Conditions

Samples	Temp. (°C)	Time (h)	Molar ratio ^a	DS
CC1	25	14	9	0.18
CC2	45	14	9	0.29
CC3	50	14	9	0.34
CC4	60	14	3	0.14
CC5	60	14	6	0.25
CC6	60	14	9	0.46
CC7	60	14	12	0.50
CC8	60	4	9	0.34
CC9	60	8	9	0.44

^aThe molar ratio of CHPTAC to AGU.

was neutralized with aqueous acetic acid and then dialyzed with a regenerated cellulose bag (M_w cutoff 8000) against distilled water for about 7 days. The solution was finally freeze-dried to obtain the purified CC.

Grafting of CC with PAM in Homogeneous Conditions

The mixture of CC and distilled water was placed in a four-neck flask equipped with a mechanical stirrer, reflux condenser, thermometer, and nitrogen line. The flask was immersed in a water bath and preheated at a certain temperature. Nitrogen gas was bubbled into the solution for 30 min. Then a predetermined amount of APS solution was added. After 15 min of stirring, PAM was added to the mixture. The polymerization was conducted under constant stirring and purging for 1 h. After the reaction, the product was precipitated with excess 95 wt % ethanol to dissolve PAM.¹⁹ Then the product was washed with anhydrous ethanol and dried at 50°C for 12 h to obtain the cationic cellulose-graft-polyacrylamide flocculant (CC-g-PAM). The grafting ratio (GR) was measured gravimetrically and defined as the mass ratio between grafted monomer and initial substrate.

Intrinsic Viscosity Measurement

Viscosity measurement of the CC-g-PAM solution was carried out with an Ubbelohde viscometer (SUNLEX, Shanghai, China) according to GB/T 12005.1-1989. The viscosities were measured in NaCl aqueous solutions. The intrinsic viscosity was obtained by plotting η_{sp}/C versus C and $\ln\eta_{sp}/C$ versus C and then taking the common intercept at $C=0$ of the best-fit straight lines from the two sets of points.

Elemental Analysis

The nitrogen content (N %) of CC was measured with an elemental analyzer (VARIO EL cube, Elemental Analysis System Co., Hanau, Germany). The degree of substitution (DS) was calculated from the nitrogen analysis according to the following equation⁶:

$$DS = \frac{162N\%}{14 - 151.5N\%} \quad (1)$$

where 162 is the molar mass of the anhydroglucose unit (AGU), 14 is the atomic weight of nitrogen, and 151.5 is the molecular weight of the cationic substituting group.

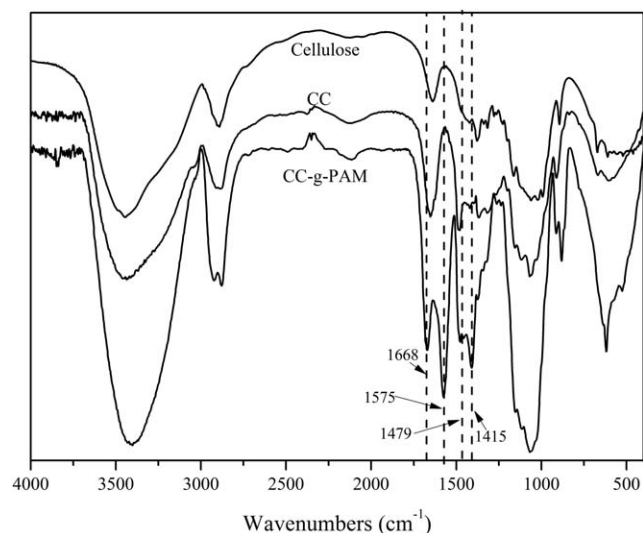


Figure 1. FTIR spectra of cellulose, CC (CC7), and CC-g-PAM (CC-g-PAM 4).

FTIR Spectroscopy

The infrared spectra of the CC and CC-g-PAM were characterized by using a Fourier transform infrared spectrophotometer (TENSOR27, Bruker, Woodlands, Texas, USA). All measurements were carried out using the KBr disk technique.

NMR Spectroscopy

$^1\text{H-NMR}$ measurements of the samples in D_2O at 25°C were carried out on a VANCE III400 spectrometer (Bruker, Woodlands, Texas, USA), operating at 500 MHz, and the sample concentration was about 1.5 wt %. The chemical shifts were referenced to the signals of tetramethylsilane (TMS).

Flocculation Test

The zeta potential of kaolin suspensions was measured using a Nano ZS ZEN3600 (Malvern, UK). The flocculation properties of the flocculant were investigated using 0.20 wt % of a kaolin suspension with a turbidity meter. The suspension was stirred at a constant speed of 200 rpm for 3 min, followed by low stirring at 40 rpm for 5 min. The flocculant was then left to settle for 15 min. At the end of the settling period, clean supernatant liquid was drawn from a depth of 1 cm, and its turbidity was measured using the turbidity meter, and the turbidity removal (TR) was calculated according to the following equation:

$$\text{TR}\% = \frac{T_i - T_f}{T_i} \quad (2)$$

where T_i and T_f are the turbidities of the initial suspension and supernatant (NTU), respectively.

RESULTS AND DISCUSSION

FTIR

Figure 1 shows the FTIR spectra of cellulose, CC, and CC-g-PAM. The spectrum of the cellulose showed the peak at about 3447 cm^{-1} that is attributed to the hydroxyl stretching vibration of cellulose. The peak at 1640 cm^{-1} corresponds to the hydroxyl stretching vibration of adsorbed water. The peaks observed at 1378 , 1316 , 1157 , 1061 , 1030 , and 892 cm^{-1} are related to functional groups of cellulose.²² The spectrum of the CC showed an additional peak at 1479 cm^{-1} , which corresponds to the methyl

groups of ammonium.²³ The peak at 1415 cm^{-1} was assigned to the C—N stretching vibration.²⁴ It indicated that the CHPTAC was successfully introduced onto the cellulose backbone. The spectrum of the CC-g-PAM showed that the characteristic peaks of CC-g-PAM are different from cellulose. The greatest difference between the CC and CC-g-PAM spectra was demonstrated by the peaks of CC-g-PAM at 1668 and 1575 cm^{-1} , which confirmed the presence of amide groups.²⁵ The peaks at 1157 , 1120 , and 1061 cm^{-1} are due to CHO—CH₂ stretching.²⁶ It was observed that almost all the characteristic peaks of CC and PAM are present in the FTIR spectrum of CC-g-PAM.

$^1\text{H-NMR}$

Figure 2 shows a typical $^1\text{H-NMR}$ spectra of the CC and CC-g-PAM in D_2O . The spectrum of CC shows a strong peak at 3.17 ppm, which is related to the methyl protons of the ammonium group. The peaks from 3.2 to 4.0 ppm can be assigned to the other protons on the cellulose backbone and substitution groups.¹¹ In comparison with the spectrum of the BC, the spectrum of the CC-g-PAM shows some additional peaks from 2.73 to 1.10 ppm, which are attributed to the acrylamide group.

Preparation of CC

Generally, CHPTAC can be converted to its epoxide form (2,3-epoxypropyl trimethylammonium chloride) under alkaline conditions, and then the epoxide form of CHPTAC reacts with cellulose to yield CC (Scheme 1).²⁶ The detailed reaction conditions and the DS values of CC are summarized in Table I. The DS value of the CC increased with increasing reaction time, as well as the molar ratio of CHPTAC to AGU, which agrees well with the values reported in the literature.²⁷ Song *et al.* found that the etherification of cellulose is hardly affected by the reaction temperature.²⁷ However, in this study, the DS value of the CC increased with increasing reaction temperature, which was different from the result of Song *et al.* The reason for the difference was that the cellulose concentration was 2% in Song *et al.*, and further increases in temperature could result in the gelation of the cellulose solution because when the cellulose concentration is above 2% it is very likely to gel.¹²

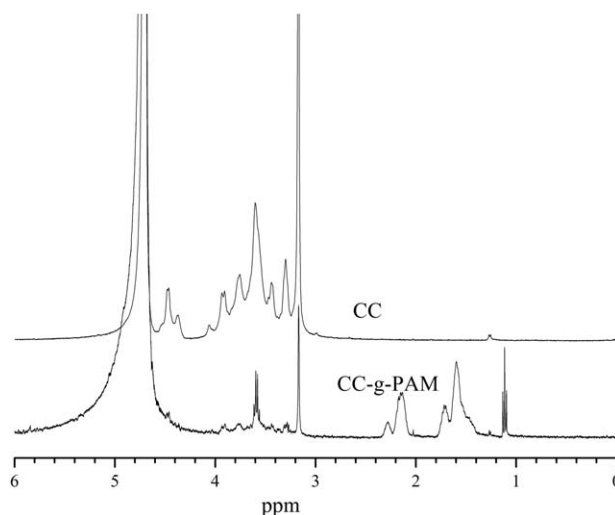
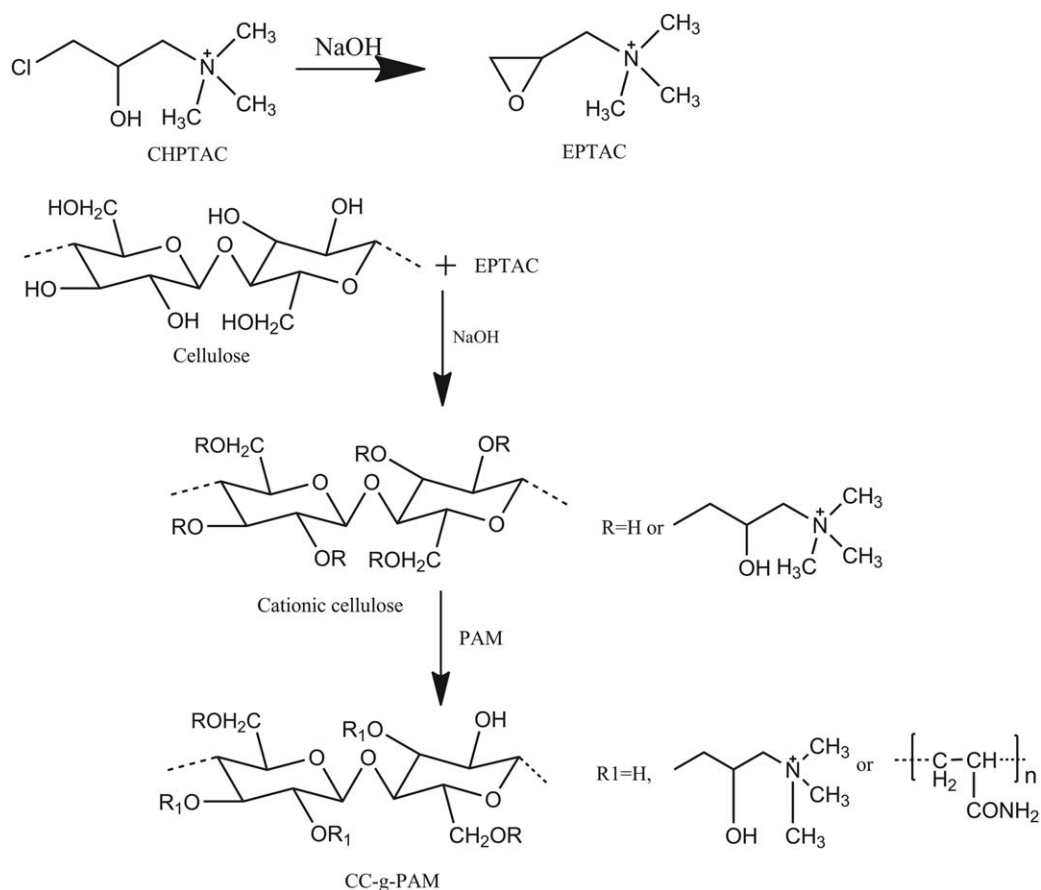


Figure 2. $^1\text{H-NMR}$ spectra of CC (CC7) and CC-g-PAM (CC-g-PAM 4) in D_2O at 25°C .



Scheme 1. Representation for the synthesis of CC-g-PAM.

Synthesis Conditions of CC-g-PAM

In order to study the efficiency of synthesis conditions on the TR and GR of CC-g-PAM, CC7 was selected as the synthetic raw material and a series of experiments were performed; the

results are presented in Table II. The TR and GR remarkably increased as the reaction temperature increased from 40 to 55°C. A further increase in the reaction temperature to 70°C resulted in a very slight decrease in the TR. Generally, the

Table II. Effect of Synthesis Conditions on the TR and GR of CC-g-PAM

Run	PAM conc. ^a (w/w)	Initiator conc. ^b (w/w)	Temp. (°C)	TR (%)	GR (%)
CC-g-PAM 1	1	0.25	40	37.92	24.63
CC-g-PAM 2	1	0.25	45	34.84	28.41
CC-g-PAM 3	1	0.25	50	62.55	41.58
CC-g-PAM 4	1	0.25	55	95.84	51.24
CC-g-PAM 5	1	0.25	60	87.32	53.27
CC-g-PAM 6	1	0.25	70	79.28	48.69
CC-g-PAM 7	1.4	0.25	55	43.66	26.57
CC-g-PAM 8	1.2	0.25	55	75.08	33.89
CC-g-PAM 9	0.8	0.25	55	88.83	49.14
CC-g-PAM 10	0.6	0.25	55	54.75	40.02
CC-g-PAM 11	1	0.1	55	36.71	19.68
CC-g-PAM 12	1	0.15	55	42.66	26.86
CC-g-PAM 13	1	0.2	55	67.83	46.84
CC-g-PAM 14	1	0.4	55	93.99	50.96

^a The mass ratio of PAM to CC.

^b The mass ratio of APS to CC.

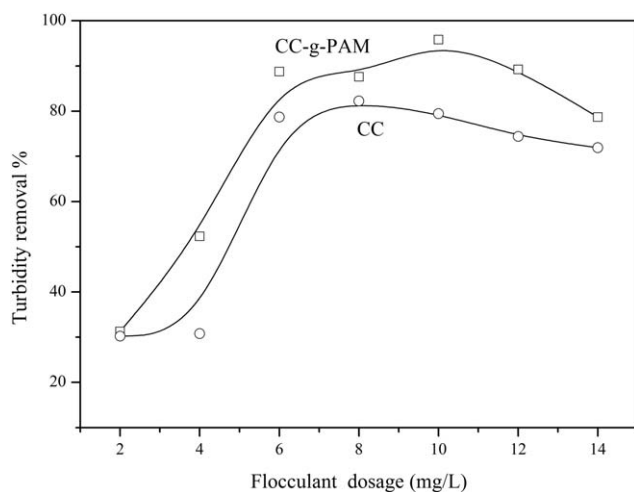


Figure 3. Flocculation efficiencies of CC (CC7) and CC-g-PAM (CC-g-PAM 4) in kaolin suspension at different flocculant dosages (pH = 7).

decomposition rate of APS accelerates with the increase of temperature, generating more reactive sites on the cellulose backbone. Thus, the initiation rate and propagation rate of the grafting reaction has been accelerated. However, at higher temperatures, the TR decreases, which may be due to the hydrolysis of PAM taking place at higher temperature. It is also clear from Table II that the TR and GR increase with an increasing amount of initiator. It is possible that more grafting sites are initiated as the APS concentration increases. The TR increased first and then decreased with an increase in the PAM concentration. This may be because an increase in the PAM concentration leads to the accumulation of AM molecules, which is in close proximity to the polymer backbone, so the PAM chains are grafted onto the CC skeleton by free-radical graft copolymerization, with the increase of the formed C—O—C groups.¹⁶

Flocculation Efficiency

Figure 3 shows the flocculation efficiencies of the CC and CC-g-PAM in a kaolin suspension at different flocculant dosages. It

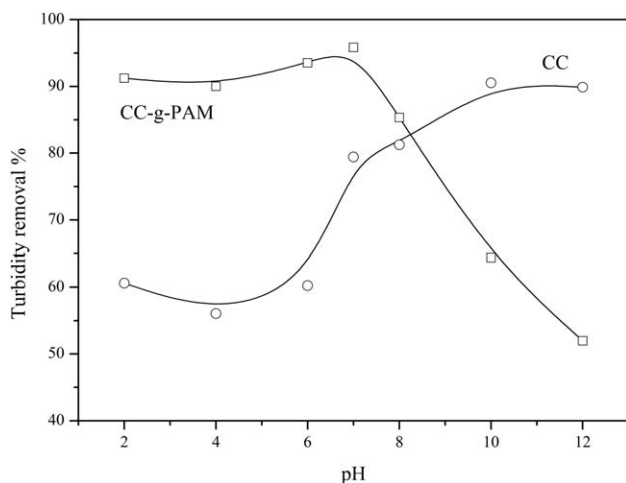


Figure 4. Flocculation efficiencies of CC (CC7) and CC-g-PAM (CC-g-PAM 4) in kaolin suspension at different pH values (flocculant dosage: 10 mg/L).

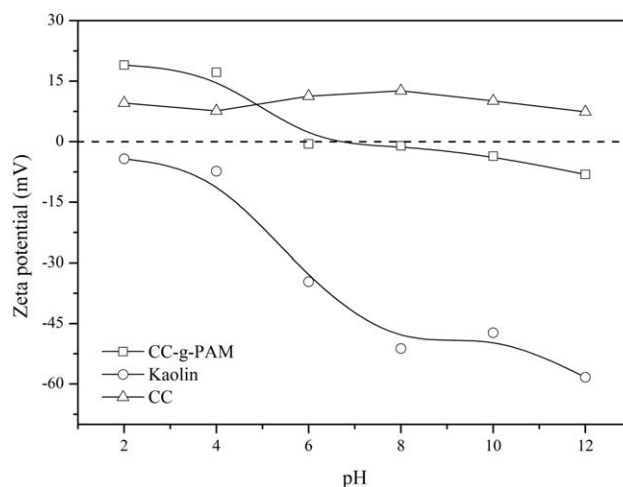


Figure 5. Zeta potential of kaolin suspension CC (CC7) and CC-g-PAM (CC-g-PAM 4) solution (10 mg/L) at different pH values.

has been observed that the CC-g-PAM shows the better flocculation efficiency than the CC at all flocculant dosages. The TR of the CC-g-PAM and CC increased first and then decreased with increased dosage of flocculants. This might be explained by the fact that the number of active binding sites present for effective bridging on the particle surface is higher at moderate flocculant concentration than at lower concentration. On the other hand, at higher polymer concentrations, the number of tails and loops accessible for bridging are decreased, which retards the flocculation performance because of the higher surface coverage and the strong electrostatic repulsion between the similarly charged polymer and particles.²⁸

Figure 4 shows the influence of pH on the flocculation of CC and CC-g-PAM to the kaolin suspension. At lower pH, the CC-g-PAM showed a good flocculation efficiency (in the range of pH 1–7), the TR was very high, and about 90% of the kaolin suspension was removed. However, the TR declined with increasing pH value. Song *et al.* have described a similar phenomenon.¹² In contrast, the CC showed good flocculation performance under alkaline conditions, and the TR increased significantly with increasing pH value. Figure 5 represents the pH dependence of the zeta potential for the kaolin suspension, CC, and CC-g-PAM. It can be seen that the kaolin suspension is negatively charged over the entire pH range, while the zeta potential of CC is positively charged over the entire pH range. The zeta potential absolute value of the kaolin suspension increased with an increase in pH value of the solution. Thus, it can be concluded that the charge neutralization mechanism is the major mechanism for the CC system.

The CC-g-PAM solution has an isoelectric point at pH 6 and presents a positive charge below the isoelectric point, and the zeta potential of CC-g-PAM decreased with increasing pH value. In the pH range below the isoelectric point (<6), due to the existence of electrostatic attraction between the positively charged CC-g-PAM and negatively charged kaolin suspension particles, the charge neutralization effect predominates, which results in better flocculation characteristics,¹⁸ and these conditions may be beneficial to the bridging effect of the interacting

particles as well.¹² However, the negative surface charges on the CC-g-PAM increased when the pH value was above the isoelectric point of CC-g-PAM. It well known that the concentration of OH⁻ increases with increasing pH value, so adsorption of OH⁻ ions on the CC-g-PAM interface results in a large diffuse double layer having a negative zeta potential value.²⁹ Consequently, the electrostatic repulsion between the flocculants and the suspended particles was increased. The intrinsic viscosity of the CC-g-PAM was 10.87 dl/g. Generally, the intrinsic viscosity is a function of the polymer molecular weight. A polymer with longer branches will have higher intrinsic viscosity and vice versa. Thus, it can be concluded that in acidic pH the charge neutralization effect was favor in the flocculation mechanism, while under neutral or alkaline conditions, the bridging effect plays an important role, making the particles cluster on the surface of the CC-g-PAM flocculant.

CONCLUSIONS

Water-soluble CC was successfully synthesized by the reaction between microcrystalline cellulose and CHPTAC in a NaOH/urea aqueous solution. The DS value of the CC was increased with an increasing molar ratio of CHPTAC to AGU. Furthermore, the CC-g-PAM flocculants were successfully synthesized by the reaction between CC and PAM in a homogeneous aqueous solution. The flocculation properties of the CC and CC-g-PAM were investigated by a jar test procedure using the kaolin suspension. The CC-g-PAM appeared to have an isoelectric point at pH 6 and showed a negative zeta potential above the isoelectric point. Under acidic and neutral conditions, the CC-g-PAM presented the better flocculation capability for the kaolin suspension, while the CC showed better flocculation performance under alkaline conditions.

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