Synthesis and Flocculation Behavior of Cationic Konjac Glucomannan Containing Quaternary Ammonium Substituents

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ABSTRACT: A quaternary ammonium derivative of konjac glucomannan (KGM) was prepared by a dry process from KGM and 2,3-epoxypropyl trimethylammonium chloride. We determined the optimization of the experimental conditions by studying on the effects of the water amount, alkaline catalyst amount, reaction temperature, and reaction time on the degree of substitution. In addition, the flocculation characteristics of the cationic derivative of KGM were evaluated in a 1.0% kaolin suspension with spectrophotometry via investigation of the influence of the flocculant amount, pH, salt concentration, temperature, and settling time on the flocculation. The results show that the synthesized cationic KGM could potentially be used as a high-performance flocculating agent. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2368–2374, 2010

Key words: biopolymers; functionalization of polymers; polysaccharides

INTRODUCTION

Anionic, cationic, and nonionic polymeric flocculants endowed with several distinguishing characteristics are being increasingly applied to the treatment of industrial effluents and municipal wastewater. Recently, flocculants based on natural polymers, which are pollution-free, biodegradable, and low-cost and have a wide range of applications, have attracted much attention from many researchers. A large amount of work has been carried out to develop flocculants based on starch,[1–3] chitosan,[4,5] cellulose,[6,7] guar gum,[8] and other natural polymers. Konjac glucomannan (KGM), a neutral polysaccharide, is the main component of the tuber of *Amorphophallus konjac C. Koch.* It consists of β-1,4-linked D-mannose and D-glucose in an approximate ratio of 2 : 3. Because the hydrosol of KGM has a high viscosity and a variety of features, such as thickening, gelling, and filming properties, KGM has broad applications in medicine, textiles, petroleum, chemical, food, and other fields. The study of KGM and its modified products has become a hot spot for a large number of researchers, including our group.[9–18] Although some researchers[17] have reported on the phosphate modification of KGM to prepare flocculants, in general, research into flocculants based on KGM has been relatively rare. Recently, flocculants based on graft copolymers of KGM with acrylamide have been reported.[19,20] However, these kinds of products are nonionic flocculants, so they show poor effects on the sludge-containing negative charge. As it is well known, most wastewater and industrial effluents contain high contents of organic materials or colloidal clays, and the surfaces of their particles are negative, on which most anionic or nonionic polymer flocculants are not effective. Apparently, cationic polysaccharides are effective flocculants for highly negative waste suspensions through adsorption and neutralization or through adsorption and bridging of two negatively charged colloidal particles and other pollutants. As a result, cationic flocculants have concerned many researchers.

Recently, Yu et al.[21] reported a cationic derivative of KGM by reacting KGM with 3-chloro-2-hydroxypropyltrimethylammonium chloride in aqueous solution. However, they evaluated the rheological properties and antimicrobial activity of the cationic KGM. As a result, they neither reported the synthetic conditions in detail nor examined the flocculation characteristics of the derivatives. Accordingly,

in this study, we dealt with the preparation a kind of cationic KGM derivative by a dry process from KGM and 2,3-epoxypropyl trimethylammonium chloride (EPTMAC), attempted to investigate the influence of the synthetic conditions on the degree of substitution (DS) of KGM, and studied the flocculation properties of cationic KGM.

EXPERIMENTAL

Materials

KGM, supplied by Hubei Hongye Konjac Co. (Enshi, China), was purified with ethanol and then dried under reduced pressure until it reached a constant weight. EPTMAC, chemically pure, was provided by Huahao Chemical Co. (Shanghai, China). Kaolin, an industrial product, was purchased from Suzhou Kaolin Production Co. (Suzhou, China). Other reagents were analytically pure and were used as received without further treatment.

Synthesis of cationic KGM by a dry process

A certain amount of NaOH (after grinding) was added to a certain amount of KGM (a small amount of water was added in advance to maintain a suitable moisture content) for 15 min with mechanical stirring. EPTMAC was added to the previous mixture at room temperature, thoroughly mixed for 15 min, and kept in a thermostated water bath for a certain time and a certain temperature. At the end of reaction, the reaction mixture was acidified with ethanol-containing acetic acid and then filtered and washed with a mixture of ethanol and water (85 : 15 v/v) until the filtrate was free of chlorine ions. The products were dried *in vacuo* at 40°C for 24 h to a constant weight.

DS

The extent of amination was traced by determination of the nitrogen content (N %) with the semi-micro Kjeldahl method. The nitrogen content ($N\%$) was determined according to the following equation:[22,23]

$$N\% = \frac{1.401 \times c \times (V_1 - V_0)}{m_0} \times 100$$

where V_1 and V_0 are the volumes of the consumed HCl standard aqueous solution (mL) for the titration of the samples and the blank, respectively; m_0 is the dry weight of the sample; and c is the concentration of the HCl standard aqueous solution (mol/L).

The DS for cationic KGM bearing quaternary ammonium groups was calculated from the following equations:[22,24]

$$DS = \frac{162.15 \times (N\%)}{1401 - 151.64 \times (N\%)}$$

where $N\%$ is the nitrogen content.method.

Fourier transform infrared (FTIR) analysis

FTIR spectra of the samples were taken by an Avatar 370 of Thermo Nicolet (Madison, WI) with the KBr disc method.

Flocculation experiments

The cationic KGM derivatives (0.5 g) were dissolved in 100 mL of deionized water with stirring for 30 min, and a 0.5% (w/v) solution was used for the flocculation experiments.

Kaolin (0.5 g) was dispersed in a 250-mL beaker with 150 mL of water with ultrasonic treatment for 15 min, followed by vigorous stirring for 1 h. A solution of cationic KGM was added at different doses, and then, water was poured to get exactly 200 mL (the final concentration of kaolin in the dispersion was 1.0 wt %). After addition of the flocculant, the suspension was stirred at a constant speed of 400 rpm for 30 s, followed by 250 rpm for 1–4 min. The flocs were then allowed to settle down for predetermined time periods. Then, the absorbency of the supernatant liquid was measured at 550 nm[25] with a spectrophotometer (Spectrophtotmeter-722, Xiamen Xingao Instruments Factory, Xiamen, China). Flocculation efficiency (FE) was calculated according to the following formula:[2,25]
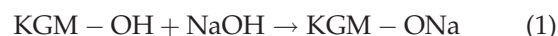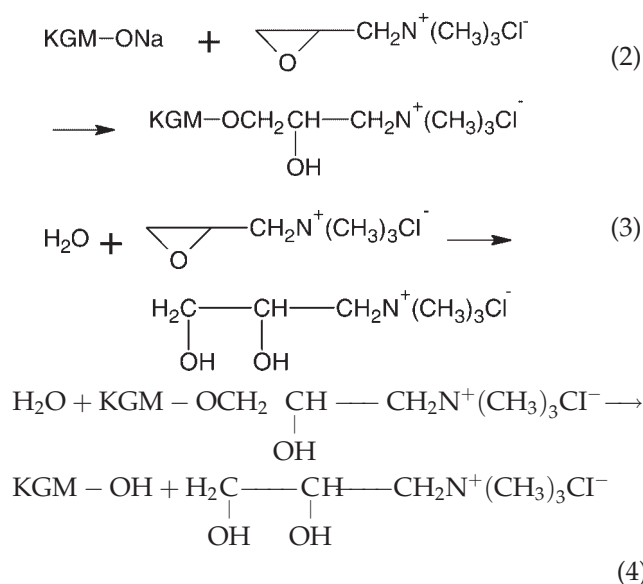
$$FE = \frac{A_0 - A_1}{A_0} \times 100\%$$

where A_1 and A_0 are the absorbencies of the clarified layer after and before flocculation, respectively.

RESULTS AND DISCUSSION

Effect of the amount of NaOH on DS

The synthesis reactions of KGM and EPTMAC are shown in the following scheme:

$$KGM - OH + NaOH \rightarrow KGM - ONa \quad (1)$$

$$KGM-ONa \quad + \quad \underset{O}{\triangle}-CH_2N^+(CH_3)_3Cl^- \qquad (2)$$

$$\longrightarrow \quad KGM-OCH_2\underset{\underset{OH}{|}}{CH}-CH_2N^+(CH_3)_3Cl^-$$

$$H_2O \quad + \quad \underset{O}{\triangle}-CH_2N^+(CH_3)_3Cl^- \quad \longrightarrow \qquad (3)$$

$$\underset{\underset{OH}{|}}{H_2C}-\underset{\underset{OH}{|}}{CH}-CH_2N^+(CH_3)_3Cl^-$$

$$H_2O + KGM - OCH_2\underset{\underset{OH}{|}}{CH}---CH_2N^+(CH_3)_3Cl^- \longrightarrow$$

$$KGM - OH + \underset{\underset{OH}{|}}{H_2C}---\underset{\underset{OH}{|}}{CH}---CH_2N^+(CH_3)_3Cl^-$$

$$(4)$$

where eqs. (1) and (2) show the dominant reactions and eqs. (3) and (4) show the side reactions.

The influence of the amount of NaOH as a catalyst on the reaction is shown in Figure 1, where the other conditions are fixed. As shown in Figure 1, DS increased with increasing amount of catalyst. Because NaOH changed KGM-OH (hydroxy groups of KGM) into the strongly alkaline and nucleophilic KGM-ONa (sodium alkoxide of KGM), this favored the substitution reaction of eq. (2), and DS was enhanced. However, an excessive amount of NaOH decreased DS. Excessive alkali sped the decomposition reaction of the epoxy and quaternary ammonium of the etherifying agent and also made the KGM partially gelatinizing, which led the base to not be distributed evenly, and it was difficult for the etherifying agent to penetrate the inside of KGM. Therefore, the appropriate amount of NaOH was 30%.
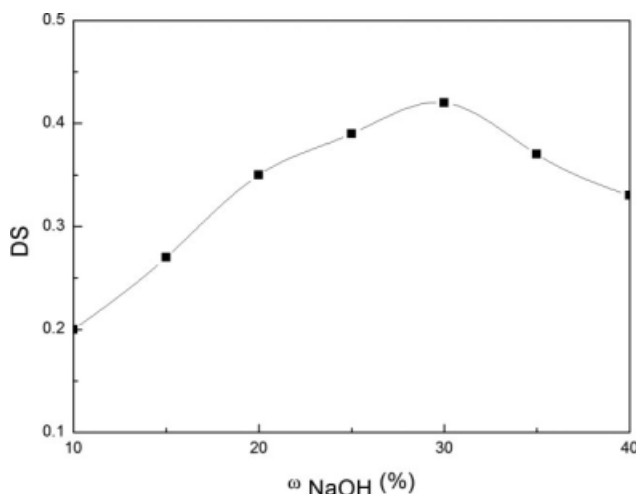

Figure 1 Effect of the amount of NaOH (ω_{NaOH}) on DS (50% EPTMAC, 20% water, 80°C, 4 h).
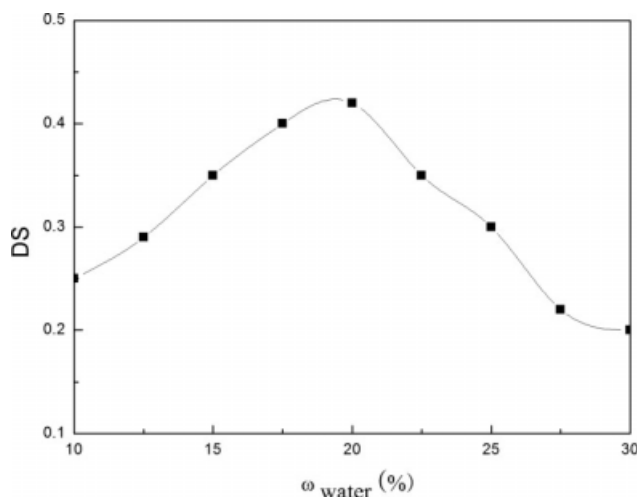
Figure 2 Effect of amount of water (ω_{water}) on DS (50% EPTMAC, 30% NaOH, 80°C, 4 h).

Effect of the amount of water on DS

The effect of the amount of water on the reaction is shown in Figure 2. As it is well known, during the drying process, a certain amount of water in the system favors the diffusion and permeation of both the catalyst and the etherifying agent inside the hydrysol of KGM and, thus, an enhancement of DS. However, as the amount of water was too high, on the one hand, the side reactions of both eqs. (3) and (4) sped up so that the effective concentration of the cationic agent in the reaction system decreased and then lowered DS. In the meantime, on the other hand, the decomposition of the generated cationic KGMs resulted in the decline of DS. With the increase in the process of the reaction, the excessive water increased the viscosity of the reactants, which produced a lump of reactants and water and made it preparation and posthandling difficult. The experiments showed that the optimum amount of water in the initial system was 20% when other conditions were fixed. As it is well known, KGM, as a type of watersoluble polysaccharide, has the ability to absorb a large amount of water, whose weight is more than several hundred times its own weight. As a result, 30 wt % of water, based on the KGM used in this system, was relatively small and appropriate.

Effect of the temperature on DS

Figure 3 shows the influence of the reaction temperature on the reaction. With increasing temperature, DS increased. This was attributed to the following: the increasing temperature favored the expansion of KGM particles and increased the collision opportunities of the reactant molecules. However, when the temperature was higher than 80°C, DS decreased because of the side reactions of both eqs. (3) and (4).
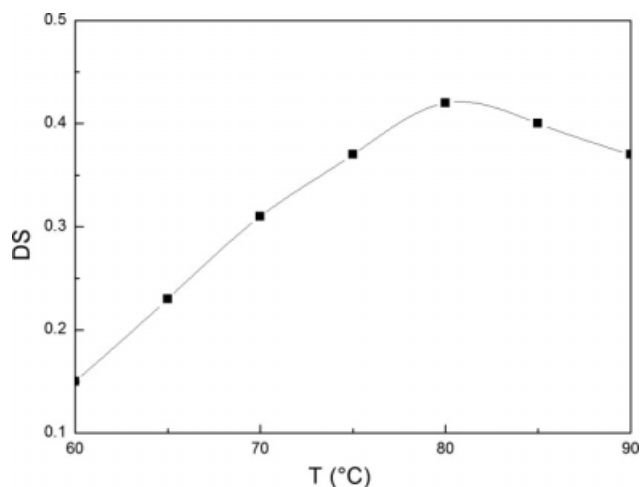
Figure 3 Effect of temperature (T) on DS (50% EPTMAC, 20% water, 30% NaOH, 4 h).

Effect of the time on DS

The impact of the reaction time on the reaction is shown in Figure 4. As shown in Figure 4, DS increased with increasing time and was relatively high when the reaction time was 4 or 5 h. However, if the reaction time was extended, there was no apparent increase in DS. As a result, the reaction time was scheduled for 4 h in consideration of the best ratio of time to efficiency.

Effect of the etherifying agent on the reaction

The influence of the weight ratio of etherifying agent to KGM is shown in Figure 5. We can see from Figure 5 that with increasing amount of etherifying agent, DS increased remarkably at first and then decreased gradually. On the one hand, as the amount of etherifying agent increased, the amount
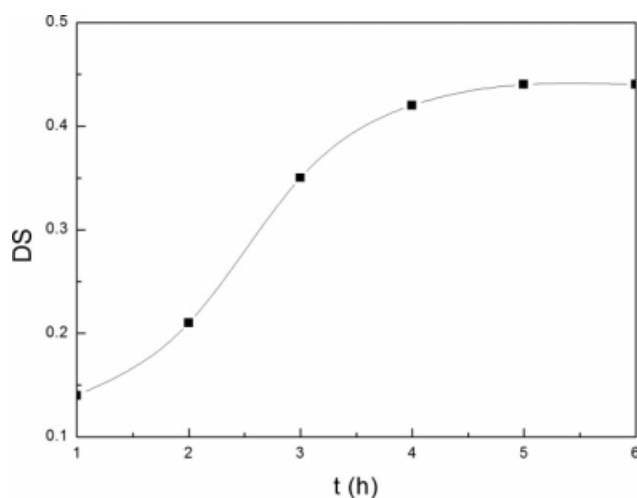

Figure 4 Effect of time (t) on DS (50% EPTMAC, 20% water, 30% NaOH, 80°C).
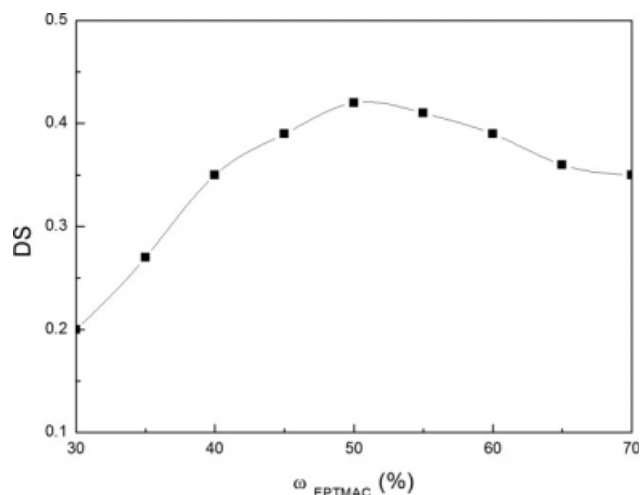

Figure 5 Effect of amount of EPTMAC (ω_{EPTMAC}) on DS (20% water, 30% NaOH, 80°C, 4 h).

of EPTMAC that took part in the reaction with the KGM molecules increased; this led DS to rise dramatically. On the other hand, with increasing amount of EPTMAC, the opportunities for side reaction increased, and then, DS dropped gradually. Therefore, the best amount of etherifying agent (e.g., 50%) was determined according to the DS of cationic KGM, to obtain the best cost-effective ratio.

Spectra of KGM and cationic KGM

The FTIR spectra of KGM and cationic KGM are shown in Figure 6(a,b), respectively. The broad band [Fig. 6(a)] at 3400 cm^{-1} was due to the stretching mode of the O—H groups. Intense bands at 1728 and 1637 cm^{-1} were for the first overtone of O—H bending vibration and the intramolecular hydrogen bonds, respectively. The bands at 1160 and 2927 cm^{-1} were assigned to C—O stretching and C—H stretching, respectively. Two strong bands at 1091 and 1018 cm^{-1} were attributed to C—O—C stretching vibrations. Figure 6(b) shows the FTIR spectrum of cationic KGM. In addition to the bands described for
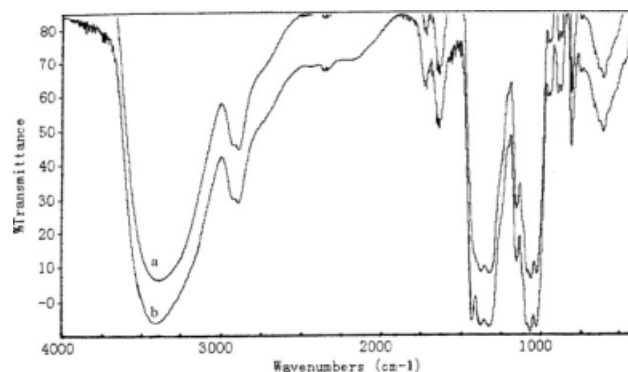

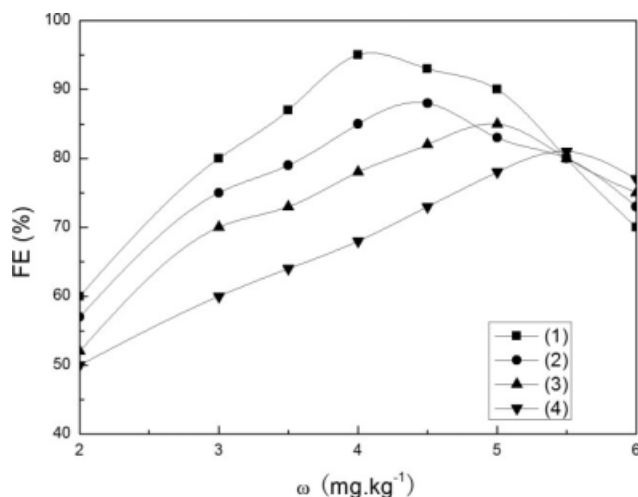**Figure 6** Spectra of (a) KGM and (b) cationic KGM.

Figure 7 Effect of the flocculant dosage and DS on FE (25°C, pH 5.0, 10 mmol/L NaCl): DS = (■) 0.42, (●) 0.35, (▲) 0.25, and (▼) 0.15. w, weight ratio of flocculant to kaolin suspension.

the KGM spectrum, the presence of an additional band at 1404 cm^{-1}, assignable to the C—N stretching vibration,[8] which was not present in KGM, was clear proof of the incorporation of a cationic moiety into the backbone of KGM.

Effects of the flocculant dosage and DS on FE

As shown in Figure 7, FE increased with increasing flocculant dosage, then reached a maximum value, and afterward, decreased. These results can be explained with the view of the role of charge neutralization and bridging. On the one hand, according to reports,[21,26] the isoelectric point of kaolin is about 2.5. Namely, at pH < 2.5, kaolin particles displayed a net positive ζ potential because of the deprotonation of the surface of kaolin. At pH > 2.5, kaolin particles displayed a net negative ζ potential because of the deprotonation of the surface. The addition of cationic KGM molecules to the kaolin suspensions led to attraction between the suspended particles bearing negatively charged and cationic KGM molecules. Moreover, the cationic KGM molecules attached to the solid particles still had free active sites that could be adsorbed on the remaining free surfaces of other particles. Therefore, this process resulted in a kind of so-called bridging between solid particles and the consequent formation of large flocs having a three-dimensional network structure. When the amount of flocculant was too low, it could not form a bridge between the suspended kaolin particles; thus, the suspended particles could not be settled, and therefore, the FE was weak.

Of course, with increasing dosage of the flocculant, the cationic groups of KGM molecules fully contacted and strongly combined with the sus-

pended particles in aqueous solution, which made all of the suspended particles in water enter into the range of bridging flocculation and settle from the aqueous solution. Naturally, because of the addition of flocculants, the charge neutralization increased, which resulted in a zero value of the ζ potential of the surfaces of the suspended particles at which the maximum FE occurred. Then, when an excessive amount of flocculant was used, the surfaces of the suspended particles displayed a net positive charge, which led to electrostatic repulsion, and thus, the suspended particles became restable in the solution. In addition, with increasing flocculant, the suspended particles were occluded and enveloped by polymers, and the bridging effect became negligible. The overall result was that FE decreased.

Moreover, the influence of DS on FE is shown in Figure 7. The FE of cationic KGMs with DSs ranging from 0.15 to 0.42 were tested on Kaolin dispersions. For sample 4, the KGM of lowest cationicity (DS = 0.15), a maximum FE of 81% was obtained at a dosage of 5.5 mg/kg. In the case of the highly cationized sample 1 (DS = 0.42), a maximum FE of 95% was achieved at a dosage of 4 mg/kg, whereas samples 2 (DS = 0.35) and 3 (DS = 0.25) produced maximum results of 88 and 85% at dosages of 4.5 and 5.0 mg/kg, respectively. With increasing DS, FE increased, but the maximum dosage decreased. This phenomenon may have been due to the fact that the highly cationic density of KGM favored the bridging effect between the solid particles.

Effect of the pH value on FE

At room temperature, 0.5% kaolin suspensions with certain amounts of flocculants were prepared, and their pH values were adjusted by either NaOH or HCl. The effects of pH on the flocculating effect of cationic KGM with the best dosage is shown in Figure 8. As shown in Figure 8, the pH value of the suspension played a significant role in the flocculation process. The results show that the maximum FE occurred at pH 5; however, with either pH < 5 or pH > 5, FE of the cationic KGM decreased. As is well known, the pH in a suspension determines the sign of the surface charge of the particles, can change the charge characteristics of a cationic KGM chain, and can even change the conformations of polymers in solution.[22] In acidic media, the polymer chains are easily open because of the mutual repulsion of cationic groups of cationic KGM. Moreover, the H$^+$ adsorbed on the negative kaolin particles led to a decrease in active sites of the surface of kaolin, which could be available to cationic KGM. As a result, the flocculating effect decreased. At the high pH value, because of the Coulomb force between OH$^-$ and cationic KGM, the active sites in cationic
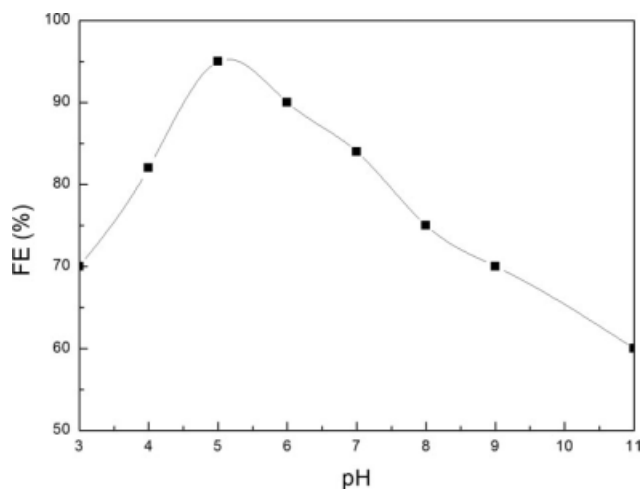
Figure 8 Effect of the pH on FE (25°C, 10 mmol/L NaCl).

Figure 10 Effect of the temperature (T) on flocculation (pH 5.0, 10 mmol/L NaCl).

KGM decreased. Therefore, the adsorption of cationic KGM molecules onto the surface of kaolin particles was inhibited, which gave rise to a decreased FE.

Effect of the salt concentration on FE

Figure 9 shows the effect of NaCl concentration on the flocculating effect in the cases of both the kaolin dosage and other conditions being fixed. In comparison with distilled water, FE was significantly enhanced with an initial increase in salt concentration, decreased slightly afterward, and then leveled off with further increases in NaCl concentration. Several researchers also observed the same phenomenon in other cationic flocculants.[2,23] The initial increase in FE might have been due to the partial neutralization of colloidal particles by Na^+ in aqueous solution, which weakened the repulsion of charges at the aggregation of kaolin particles and
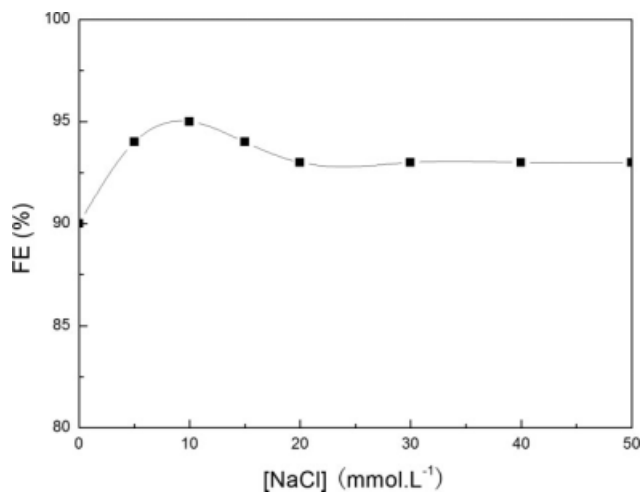
made the bridging occur more easily. However, at a too high salt concentration, the chain segments of polymers could not easily extend and become curled, which made the bridging fail and decreased FE.

Effect of the temperature on FE

The influence of temperature on flocculation was studied, as shown in Figure 10. FE increased with increasing temperature in the range 15–60°C. A large-scale study showed that in terms of cationic flocculants, the flocs became large and tight with increasing temperature. At the low temperature, the surfaces of the suspended kaolin particles were saturated by the adsorption of flocculants, and the flocs were relatively stable because of electrostatic repulsion. However, with increasing temperature, some cationic flocculants adsorbed on the surface of kaolin
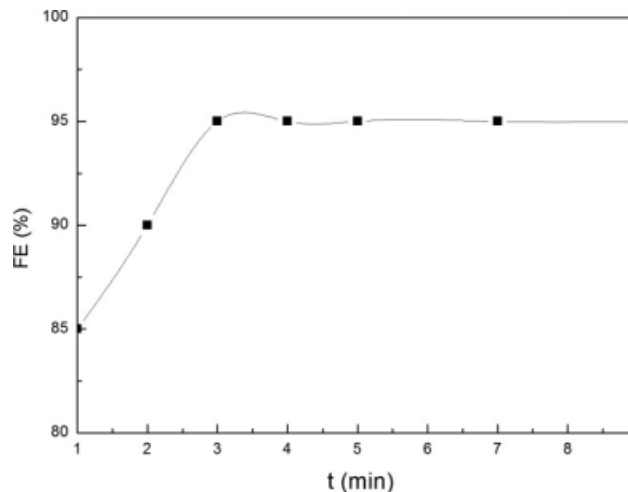

Figure 9 Effect of the salt concentration on FE (25°C, pH 5.0).

Figure 11 Effect of the settling time (t) on flocculation (25°C, pH 5.0, 10 mmol/L NaCl).

particles collapsed, which gave rise to a decrease in the steric stabilization of the flocs.

Effect of the settling time on FE

For the optimum dosage of cationic KGM, the influence of settling time on the flocculation was investigated, as shown in Figure 11. With increasing settling time, the flocculation increased, and the optimum flocculation time was found to be 5 min. If the settling time was longer than 5 min, FE almost did not change anymore. The results were attributed to the following: during the initial stage, the adsorptive rate of polymers onto the surface of particles was relatively rapid, and then, the increasing coalescence efficiency led to an increasing FE. Subsequently, the adsorption of cationic KGM onto the surface of kaolin particles decreased and reached equilibrium. It was obvious that a large number of vacant surface sites were available for adsorption during the initial stages, and after a lapse of time, the remaining vacant surface sites were difficult to occupy because of repulsive forces between cationic KGM adsorbed on the surface of the kaolin particles and solution phase.

CONCLUSIONS

The preparation conditions of cationic KGM flocculants by a dry process from natural KGM and EPT-MAC were investigated. The influence of the synthesized conditions, such as the amount of cationic reagent, amount of catalyst, reaction time, and reaction temperature, on DS have been discussed. The optimum conditions were 25 g of KGM, 50% EPT-MAC, 30% NaOH, a reaction temperature of 80°C, a reaction time of 4 h; at the optimum conditions, DS was 0.42.

Moreover, the derivatized polymer presented flocculation characteristics for a 1.0% kaolin suspension, with possible application in environmental water treatment. The effects of the amount of flocculant agent, DS of KGM, pH, salt concentration, temperature, and settling time on flocculation were also studied. The results show that the synthesized cationic derivative of KGM had good flocculation characteristics.

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