

# Flocculation Performance of Modified Chitosan in an Aqueous Suspension

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**ABSTRACT:** A cationic moiety, *N*-(3-chloro-2-hydroxypropyl)trimethyl ammonium chloride (CHPTAC), was incorporated onto chitosan in an aqueous alkaline solution. Thus, modified chitosan was prepared. A series of modified chitosans with different molecular weights and charge densities were synthesized through the alteration of the molar ratio of CHPTAC to chitosan in the reaction mixture. The synthesized modified chitosans were thereafter characterized by a variety of physicochemical characterization techniques to confirm that modification did take place. Furthermore, the feasibility of applying modified chitosans as flocculants was assessed, and they were compared with the native chitosan in model colloidal suspensions of kaolin

and iron-ore powder. The results indicated that the unmodified chitosan itself was a good flocculating agent. The flocculation performance of the chitosan could be altered by the incorporation of the CHPTAC moiety. Studies showed that not all the modified chitosans had superior flocculation performance versus the native chitosan. Among the different grades, the modified chitosan with a moderate molecular weight and a moderate charge density showed the best flocculation performance in both model suspensions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2592–2600, 2010

**Key words:** biopolymers; colloids; renewable resources; water-soluble polymers; cationic flocculant

## INTRODUCTION

The mineral and paper-processing industries require very large volumes of fresh water every day. Because fresh water has become a valuable commodity, the recycling and reuse of wastewater have become indispensable for all processing industries to reduce processing costs and also to abide by environmental rules and regulations.<sup>1</sup>

The wastewater emanating from these industries contains very fine suspended particles with sizes in the range of 0.001–10  $\mu\text{m}$ .<sup>2</sup> Because of the very small size and the presence of surface charges, it is very difficult to bring these particles closer together to create a heavier mass for settling.<sup>2</sup> Sometimes, these particles remain suspended for years.<sup>3</sup> Hence, the removal of these colloidal particles from wastewater has become a serious challenge for industry.<sup>4,5</sup>

Most of the inorganic particles carry charges in a neutral aqueous medium.<sup>6</sup> To destabilize the system, inorganic coagulants such as alum, poly(aluminum chloride), ferric chloride, ferrous sulfate, and magnesium chloride have been used for decades.<sup>7</sup> However, this process is strongly pH-dependent and

decreases the alkalinity of water.<sup>8</sup> Moreover, large amounts of inorganic coagulants are required to achieve an effective settling rate. As a result, a large volume of metal hydroxide sludge is produced. This again creates a disposal problem.<sup>9</sup> Apart from the disposal problem, the use of inorganic salts such as alum and poly(aluminum chloride) is now very controversial because of the possible impact of residual aluminum in recycled water on Alzheimer's disease.<sup>10,11</sup>

To minimize the drawbacks of inorganic coagulants, synthetic cationic flocculants are used as alternatives because of the rapid settling and lower production of sludge.<sup>12</sup> Cationic flocculants neutralize the surface charge of hydrated colloidal particles and reduce the electrical repulsion between approaching particles. Thus, the suspended particles come closer to one another. Cationic polymers also bridge the approaching particles with their long chains.<sup>13</sup> The bridging performance of cationic flocculants depends on the physicochemical properties of the polymer, such as the molecular weight, size, shape, charge density, hydrophobicity, adsorption density, and conformation of the adsorbed polymer.<sup>14</sup>

Water-soluble synthetic flocculants (mainly polyacrylamide-based cationic flocculants with different molecular weights and charge densities) have been greatly used in industry because of their economic advantages and easy tailorability.<sup>15</sup>

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However, these synthetic polymers are not biodegradable, and their degraded products are considered hazardous because of the release of monomers that could enter the food chain and cause carcinogenic effects.<sup>15,16</sup>

For these reasons, scientists around the world are trying to develop biopolymer-based cationic flocculants that have the potential to replace synthetic flocculants.<sup>17</sup>

Fanta et al.<sup>18</sup> grafted cationic moieties onto starch and assessed the flocculation properties. Jones and Jordan<sup>19</sup> grafted a cationic monomer onto starch and evaluated its flocculation performance. They concluded that the cationic starch showed better flocculation performance than the native starch in a silica suspension.

Hoover and Sinkovitz<sup>20</sup> and Levy et al.<sup>21</sup> developed cationic guar gum and studied the flocculation efficiency. The optimum flocculation dose decreased with an increase in the molecular weight of the cationic guar gum. Pal and coworkers<sup>22,23</sup> developed cationic flocculants by incorporating *N*-(3-chloro-2-hydroxypropyl)trimethyl ammonium chloride (CHPTAC), a cationic moiety, onto different polysaccharides such as starch, glycogen, and guar gum. They also showed that these cationic flocculants have comparable or better flocculation efficiency with respect to some of the commercially available synthetic flocculants in different colloidal suspensions. We are very much interested in chitosan as it is widely available in the coastal areas of India, where seafood processing is one of the major industries. Chitosan is a cationic biopolymer. It is the deacetylated derivative of chitin. Chitosan is commercially produced by an alkali treatment at an elevated temperature.<sup>24</sup> Chitin is the second most abundant biopolymer after cellulose. It is largely available in the exoskeletons of crustacean shells, such as prawns, crabs, and shrimp. Structurally, chitosan is similar to cellulose. Cellulose has a hydroxyl group at the C-2 position, whereas chitosan has an amino group at the C-2 position. Muzzarelli<sup>25</sup> described the extraction, chemistry, and application of chitin and chitosan in detail. Because of the presence of amino groups, chitosan shows some unique characteristics, such as chelation of metal ions. Because of its chelation property, extensive applications have been found for chitosan in water purification. Domard et al.<sup>26</sup> investigated the adsorption of chitosan onto kaolinite. They showed that the adsorption capacity of chitosan depends on its molecular weight and degree of deacetylation. Kawamura<sup>27</sup> suggested that chitosan could be a potent substitute for synthetic flocculants.

Sekine et al.<sup>28</sup> applied chitosan to the removal of turbidity from river water. Baohong et al.<sup>29</sup> stated that chitosan forms a chelate with metal ions and

that the chelated complex has a higher settling velocity than metal coagulants. They recommended the application of chitosan as an alternative to inorganic coagulants.

Gamage and Shahidi<sup>30</sup> evaluated the chelating capacity of chitosan and showed that chitosan could serve as an effective coagulant in removing metal ions from wastewater, especially at a neutral pH.

We tried to modify the flocculation performance of chitosan by incorporating the cationic moiety CHPTAC onto it. A series of modified chitosans (Chito-cat-1 to Chito-cat-5) were synthesized by the alteration of the CHPTAC/chitosan ratio in the reaction mixture. The synthesis and characterization of the modified chitosans are presented elsewhere.<sup>31</sup>

The main objective of this study was to evaluate the flocculation performance of these modified chitosans with native chitosan as a reference.

The flocculation performance of these polymer samples was evaluated by column testing and common jar testing in model colloidal suspensions of kaolin and iron-ore powder.

## EXPERIMENTAL

### Materials for the synthesis of the modified chitosan

Chitosan [viscosity-average molecular weight ( $M_v$ ) =  $1.24 \times 10^4$  Da, weight-average molecular weight ( $M_w$ ) =  $1.32 \times 10^4$  Da] with an 86% degree of deacetylation was a gift from the Central Institute of Fisheries Technology (Cochin, India). CHPTAC was procured from Lancaster Synthesis Co. (Morecambe, England). Analytical-grade sodium hydroxide and hydrochloric acid were procured from E. Merck, Ltd. (Mumbai, India). Isopropyl alcohol was supplied by S.D. Chemicals (Mumbai, India).

### Materials for the investigation of the flocculation characteristics

Kaolin powder (average particle size = 102 nm, specific gravity =  $3260 \text{ kg/m}^3$ ,  $\zeta$  potential =  $-0.0023 \text{ V}$  at pH 7) was supplied by B.D. Pharmaceuticals Works (Howrah, India). Iron ore (average particle size = 700 nm, specific gravity =  $3450 \text{ kg/m}^3$ ,  $\zeta$  potential =  $-0.038 \text{ V}$  at pH 7) was obtained from Joda Mines (Jharkhand, India).

### Synthesis of the modified chitosan

The modified chitosan was prepared as previously mentioned.<sup>31</sup> In a typical synthesis, chitosan (0.7 g) was mixed in distilled water (250 mL). The mixture was heated to  $33^\circ\text{C}$  under controlled stirring for 30 min, and 15 mL of 1N sodium hydroxide was added. After 15 min, an aqueous solution of

CHPTAC was added to the reaction mixture. The reaction was then allowed to continue for the next 18 h. Diluted hydrochloric acid was added to the mixture to lower the reaction pH below 7. This stopped the reaction. The modified chitosan was then precipitated in an excess of isopropyl alcohol. The precipitate was washed with isopropyl alcohol several times to remove the unreacted CHPTAC. It was then dried in a vacuum oven at 60°C for 2 h. A series of modified chitosans (Chito-cat-1 to Chito-cat 5) were thus prepared by the variation of the molar ratio of CHPTAC to chitosan in the reaction mixture (Table I).

### Characterization

Intrinsic viscosity ( $[\eta]$ ) and  $M_v$

Measurements of  $[\eta]$  were carried out with an Ubbelohde viscometer (Cannon Ubbelohde, State College, PA) at 30°C. The viscosity was measured in a dilute aqueous solution. The pH of the polymer solution was slightly acidic. The time of flow of the solution was measured at four different concentrations. From the time of flow of the polymer solutions ( $t$ ) and the time of flow of the solvent distilled water ( $t_0$ ), the relative viscosity ( $\eta_{rel} = t/t_0$ ) was obtained. The specific viscosity ( $\eta_{sp}$ ) was calculated as well ( $\eta_{sp} = \eta_{rel} - 1$ ). The reduced viscosity [ $\eta_{red} = \eta_{sp}/C$ , where  $C$  is the concentration (dL/g)] and the inherent viscosity ( $\eta_{inh} = \ln \eta_{rel}/C$ ) of the polymer samples were plotted for different values of  $C$ . The extrapolated curves met at the zero concentration. The point of intersection at the zero concentration was the measure of  $[\eta]$  for the polymer samples. The  $[\eta]$  values of the modified chitosans are summarized in Table I.  $M_v$  of the modified chitosans was derived from the  $[\eta]$  values with the Mark-Houwink equation<sup>32</sup>:

$$[\eta] = KM_v^a$$

where  $K$  and  $a$  are constants whose values depend on the polymer type and the chosen solvent.

### Gel permeation chromatography (GPC)

$M_w$  of the polymer samples was determined with a GPC system with multi-angle laser light scattering (Dawn-Eos, Wyatt Technology Corporation, Santa Barbara, CA, USA). The mobile phase was composed of a solution of 0.5M acetic acid and 0.5M sodium acetate (pH 3 acetate buffer). The solution was filtered through a nylon membrane filter before it was injected into the column. The flow rate of injection was fixed at 0.5 mL/min, and the column temperature was kept at 30°C during the analysis.

**TABLE I**  
Synthesis Details for the Modified Chitosan

Modified chitosan	CHPTAC (mol)	$[\eta]$ (dL/g)	$M_v$ (Da)	$M_w$ (Da)
Chito-cat-1	0.00175	0.32	$3.9 \times 10^3$	$4.3 \times 10^3$
Chito-cat-2	0.0030	1.51	$3.5 \times 10^4$	$3.7 \times 10^4$
Chito-cat-3	0.00426	2.443	$6.9 \times 10^4$	$7.2 \times 10^4$
Chito-cat-4	0.0054	2.736	$8.10 \times 10^4$	$8.3 \times 10^4$
Chito-cat-5	0.0061	3.245	$1.03 \times 10^5$	$1.2 \times 10^5$

### Elemental analysis

The elemental analysis was performed with a Carlo Erba 1108 elemental analyzer, Carlo Erba Instruments (Milan, Italy). The percentages of carbon, nitrogen, and hydrogen were estimated. The degree of substitution (DS) was calculated with the following relation<sup>33</sup>:

$$DS = 1/2[\text{Percentage of nitrogen} \times (\text{Molecular weight of chitosan} / \text{Molecular weight of nitrogen})]$$

The charge density of the modified chitosan was calculated with the following relation<sup>34</sup>:

$$\text{Charge density} = (1000 \times DS) / [162 + (151.64 \times DS)]$$

### IR spectroscopy

IR spectra of the virgin and modified chitosans were recorded on a PerkinElmer Cetus 630 spectrophotometer (Norwalk, C.T. USA) apparatus with the KBr pellet method. Approximately 6 mg of the dried sample was mixed with 200 mg of IR-grade KBr, and 40 mg of this mixture was used to prepare the pellet.

### $\zeta$ potential

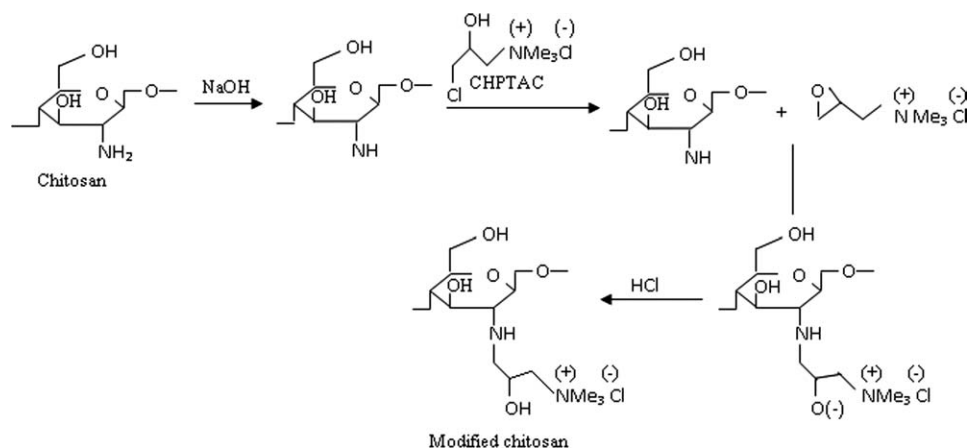
The  $\zeta$  potential of the colloidal suspensions was measured with a Zeta Meter, System 3.0 instrument (Zeta-Meter Inc., Staunton, USA).

### Flocculation studies

The flocculation performance of the polymer samples was studied with the column test and common jar test methods.

### Column test

The column test is one of the most common methods for investigating the flocculation performance. The column test used here comprised a 100-mL graduated cylinder and a stopwatch. In the column test,



**Scheme 1** Modification of chitosan with CHPTAC.

first an aqueous suspension of the colloidal particles was placed in the cylinder, and then the requisite volume of the polymer solution was added to the suspension. The cylinder was sealed, and the whole system was carefully inverted 10 times for thorough mixing (each inversion took 3 s). After that, the cylinder was kept upright, and the slurry was allowed to settle. A descending solid–liquid interface was clearly seen. The interface height of the concentrated settling solid and supernatant water was plotted against time. The settling rate of the suspension was derived from the slope of the straight-line portion of the plot of the interface height versus the settling time.

#### Jar test

A conventional jar test apparatus comprises a flocculator and a turbidity meter. The flocculator was supplied by M.B. Flocculator (Mumbai, India), and the turbidity meter was procured from Systronics (Ahmedabad, India). The flocculator consisted of six pedals of equal size on a bench that were connected to one another by a gear mechanism. The flocculator had a provision for speed control. A 400-mL aqueous suspension was placed in each 1-L beaker, and a calculated volume of the polymer solution was added to it. The mixture was initially stirred for 2 min at a constant speed of 75 rpm. At this speed, the polymer solution was thoroughly mixed in the aqueous suspension. The stirring speed was then lowered to 25 rpm, and the mixture was stirred at this particular speed for next 5 min. This allowed the polymers to be adsorbed onto the particle surface, and flocs were formed. The flocs were then allowed to settle for the next 10 min. After that, the supernatant water from each of the beakers was carefully withdrawn, and the turbidity was measured with a digital nephelometric turbidity meter.

The turbidity was expressed in nephelometric turbidity units. The relationship between the polymer dosage and the residual turbidity of the supernatant water was plotted.

## RESULTS AND DISCUSSION

### Synthesis, $[\eta]$ , and $M_v$

The modification of chitosan was performed by the incorporation of CHPTAC under alkaline conditions. Under these conditions, the CHPTAC monomer converted into the corresponding epoxide and reacted with the primary amino groups of chitosan. The synthesis process is outlined in Scheme 1.<sup>31</sup> Table I provides details for the synthetic parameters of the modified chitosan. Although a number of methods are available for incorporating cationic moieties into the backbone of polysaccharide, CHPTAC has been preferred as a cationic moiety in recent years.<sup>23</sup> Polysaccharide is an effective backbone polymer for incorporating a cationic moiety with a quaternary ammonium compound. Table I shows that with an increase in the CHPTAC/chitosan ratio in the reaction mixture,  $[\eta]$  and  $M_v$  of the modified chitosan increased. The increase in  $[\eta]$  and  $M_v$  of the modified chitosan was assumed to be due to the incorporation of an increased amount of the CHPTAC moiety onto chitosan.

### GPC

The  $M_w$  values of the polymer samples were determined by GPC and are summarized in Table I. The table shows that  $M_w$  of the modified chitosan increased with an increase in the CHPTAC content in the reaction mixture. This is in agreement with the results obtained from the  $M_v$  data. Table I shows that Chito-cat-1 had the lowest molecular weight among the modified chitosans. This was due to the

**TABLE II**  
Elemental Analysis, DS Values, and Charge Densities of the Samples

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	DS	Charge density (%)
Chitosan	40.4	6.68	7.65	—	—
CHPTAC	39.9	8.4	7.34	—	—
Chito-cat-1	40.0	8.29	7.78	0.015	1.67
Chito-cat-2	40.4	8.45	8.17	0.060	6.36
Chito-cat-3	40.2	8.47	8.34	0.078	8.27
Chito-cat-4	41.0	8.85	8.75	0.127	12.57
Chito-cat-5	40.5	8.97	8.82	0.135	13.26

presence of excess alkali in the reaction mixture, which depolymerized the chitosan backbone.

### Elemental analysis

The results of the elemental analysis of chitosan, CHPTAC, and all the modified chitosans are listed in Table II. The native chitosan contained 7.65% nitrogen. The percentage of nitrogen increased with an increase in the CHPTAC content in the reaction mixture. Table II also shows that an increase in the CHPTAC content in the reaction mixture increased both the DS and the charge density. This proved that with an increase in the CHPTAC content in the reaction mixture, more and more cationic moieties were incorporated into chitosan.

### IR spectroscopy

IR spectroscopy is one of the most common characterization tools for the investigation of chemical modification. Figure 1 shows the IR spectra of chitosan, Chito-cat-2, and the CHPTAC moiety. The IR spectrum of chitosan shows a broad O—H stretching band at  $3427\text{ cm}^{-1}$ . A peak at  $1377\text{ cm}^{-1}$  represents the C—O stretching of the primary hydroxyl group. A peak at  $1660\text{ cm}^{-1}$  represents the acetylated amine group of chitin, which indicates that the sample was not fully deacetylated. A strong bending vibration for  $-\text{NH}_2$  can be found at  $1591\text{ cm}^{-1}$ .

The IR spectrum of CHPTAC shows methyl and methylene symmetric stretching vibrations at  $3012$  and  $2837\text{ cm}^{-1}$ , respectively. A strong band at  $670\text{ cm}^{-1}$  corresponds to C—Cl stretching.

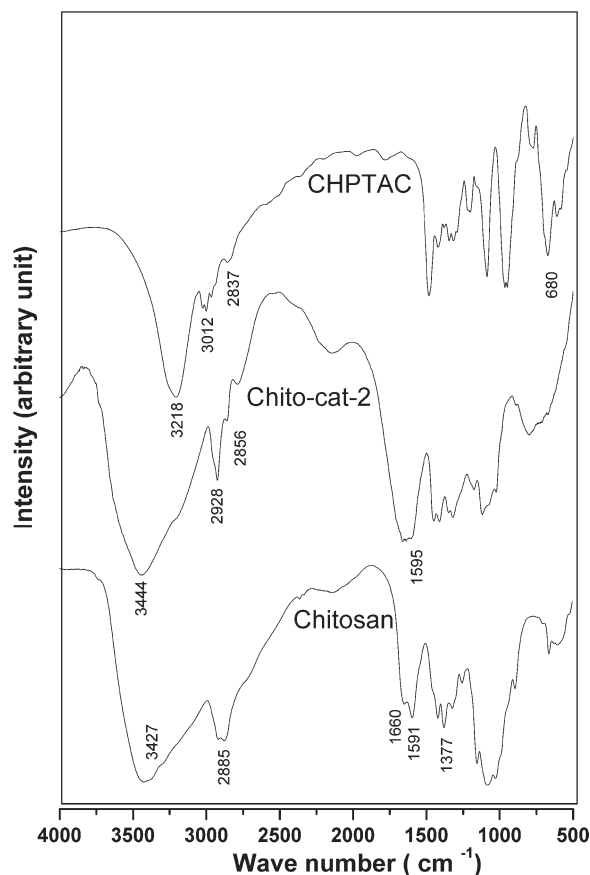
Chito-cat-2 showed a decrease in the band intensity at  $1595\text{ cm}^{-1}$  that was associated with a  $-\text{NH}_2$  bending vibration. This was a direct indication of the incorporation of the CHPTAC moiety into the primary amine group of chitosan. The appearance of intense peaks at  $2928$ – $2856\text{ cm}^{-1}$  indicates an increase in the number of methyl groups with the incorporation of the CHPTAC moiety.

### Flocculation studies

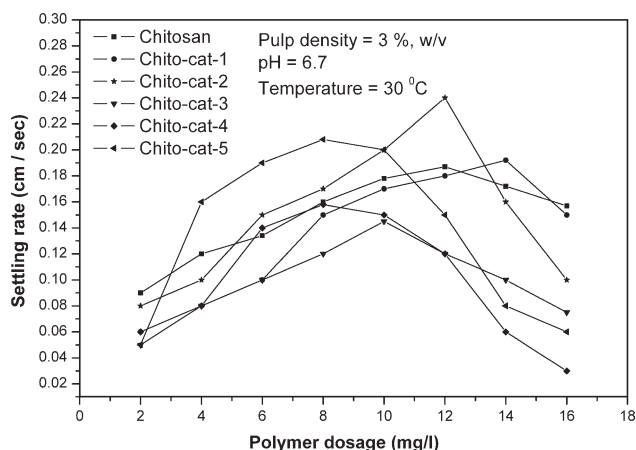
A flocculation operation generally includes both thickening of suspended solids as sludge at the bottom of the treatment tank and clarification of the supernatant liquid. Both play important roles in determining the process parameters of the flocculation operation. The column test describes how fast the polymer can thicken the suspended particles, and the jar test describes how far it can clarify the supernatant water.

### Column test

In the column test, the settling behavior of suspended particles is evaluated. It is assumed that the higher the settling rate is of the suspended particles, the better the flocculation efficiency is of the polymer used. If other conditions remain the same, the settling rate depends on the dosage of the polymer used. Figure 2 shows the settling rate of a kaolin suspension (3% w/v) with different polymers at different dosages. With an increase in the polymer dosage, the settling rate gradually increased and reached a maximum. After that, further addition of



**Figure 1** IR spectra of (a) chitosan, (b) Chito-cat-2, and (c) CHPTAC.

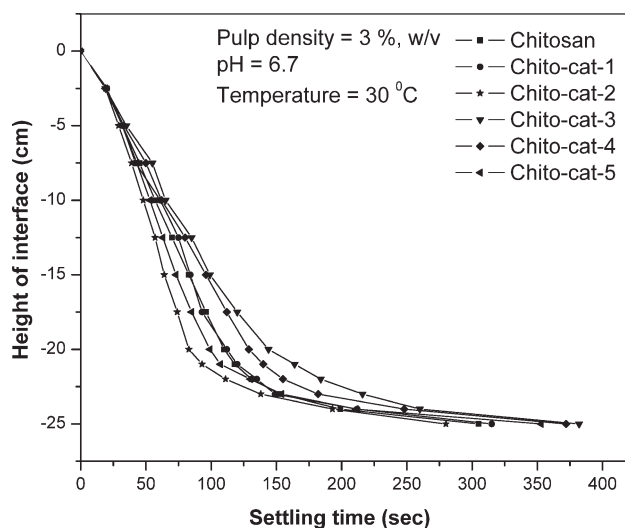


**Figure 2** Settling rate of kaolin suspensions with different polymers at different dosages.

the polymer decreased the settling rate. According to Domard et al.,<sup>26</sup> this corresponds to a progressive evolution from a partially flocculated system in the absence of the polymer to a highly flocculated medium and then to a stabilized dispersion at a higher polymer dosage. Figure 2 also shows that the highest settling rate for the kaolin suspension was obtained by Chito-cat-2 at a polymer dosage of 12 mg/L.

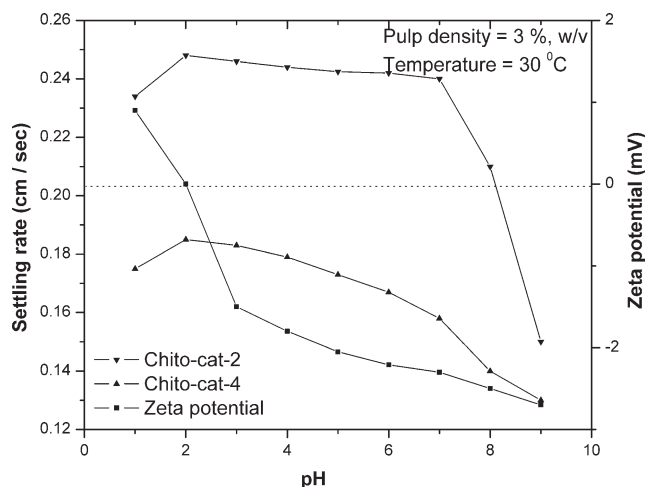
The settling behavior of the kaolin suspension (3% w/v) with different polymer samples at their optimal dosage is illustrated in Figure 3. These curves show two distinct phases of settling. The first phase had a complex pattern of accelerated settling, and the second phase showed slow settling. Closer observation revealed that in the beginning, the settling rate was relatively slow, and after that, an acceleration of the settling rate was observed. The slow settling rate at the beginning was believed to be due to the progressive growth of the flocs.<sup>35</sup> The speedup of the settling rate was attributed to the increase in the concentration of the settling solid. It was observed that in the case of the kaolin suspension, large, loosely bonded flocs were formed. During settling, they started to aggregate and released a stream of water trapped inside the flocs. This is called a channeling phenomenon. This channeling was assumed to be responsible for the speedup of the settling rate of the kaolin suspension.<sup>36,37</sup> Near the bottom of the cylinder, the concentration of the aggregates increased. This blocked the upward flow of water through the interflocs and intraflocs and lowered the settling rate.

It was anticipated that the settling performance of the modified chitosan would improve with increases in the molecular weight and charge density. However, Figures 2 and 3 show that Chito-cat-2 with a moderate molecular weight and a moderate charge density displayed better settling performance. It is

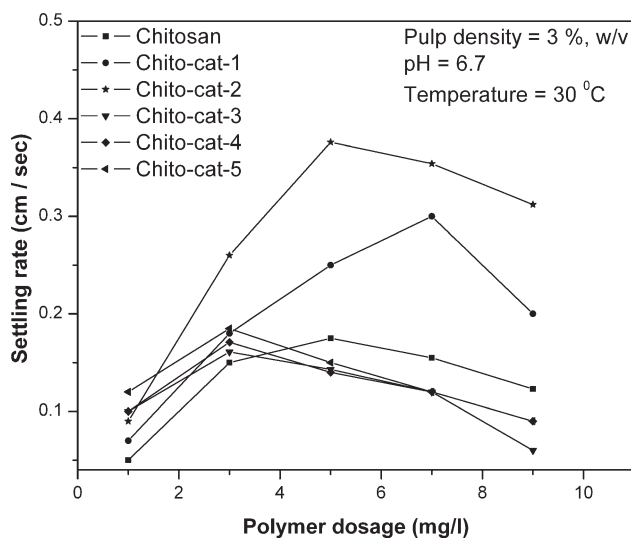


**Figure 3** Settling behavior of kaolin suspensions with different polymers at the optimal dosages.

known that the settling phenomena of suspended particles are governed by two major mechanisms: electrostatic double-layer compression or charge neutralization and polymer bridging. To determine the causes responsible for the superior flocculation performance of Chito-cat-2, the settling rate and  $\zeta$  potential of the kaolin suspension were measured as functions of pH and are presented in Figure 4. Kaolin showed an isoelectric point at pH 2; that is, at pH 2, it had no net charge on its surface. Figure 4 shows that there was no significant change in the settling rate by Chito-cat-2 at pH 2 versus the settling rate obtained at pH 7. This clearly indicates that charge neutralization was not the key mechanism for the higher settling performance of Chito-cat-2; rather, it is assumed that the better settling performance was due to the presence of large loops



**Figure 4** Effect of the pH on the settling rate and  $\zeta$  potential of kaolin suspensions.

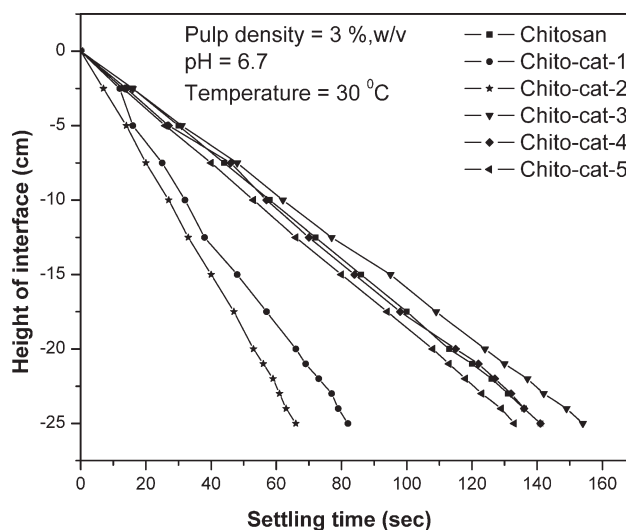


**Figure 5** Settling rate of iron-ore suspensions with different polymers at different dosages.

and tails of the Chito-cat-2 adsorbed onto the suspended kaolin surface, which extended to such a degree that they bridged a large number of neighboring kaolin particles and formed large flocs. These large flocs settled rapidly at the bottom of the settling cylinder.

On the other hand, Chito-cat-4, a modified chitosan with a higher molecular weight and a higher charge density, showed significant enhancement of the settling performance at pH 2 versus the settling performance at pH 7 (Fig. 4). This indicates that even though Chito-cat-4 had a higher molecular weight, the settling performance was primarily governed by charge neutralization rather than polymer bridging. It is assumed that for Chito-cat-3 to Chito-cat-5, a small number of polymer molecules were adsorbed onto the kaolin surface to neutralize the surface charge. This reduced the likelihood of bridging a large number of suspended kaolin particles in the aqueous suspension.

Figure 5 shows the settling rate of an iron-ore suspension (3% w/v) with different polymers and dosages. Here we can also observe that with an increase in the polymer dosage, the settling rate increased and gradually reached a maximum. After that, further addition of the polymer decreased the settling rate. Among the polymer samples, Chito-cat-2 showed better settling performance at the polymer dosage of 5 mg/L. The settling behavior of iron ore at the optimum dosages of different polymers is shown in Figure 6. The settling behavior of the kaolin suspension (Fig. 3) was significantly different from the settling behavior of the iron-ore suspension (Fig. 6). The flocs that formed with the iron-ore suspension were dense and small in size. They also tended to settle parallel to one another without inter-

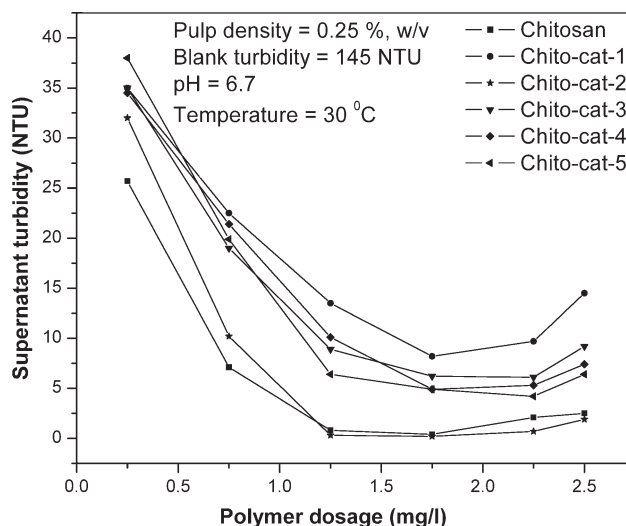


**Figure 6** Settling behavior of iron-ore suspensions with different polymers at the optimal dosages.

fering with neighboring flocs and also with uniform velocity. We assumed that because of the higher negative  $\zeta$  potential of iron ore, the polymers adsorbed onto the particle surface strongly in a flat configuration with small loops and tails. This reduced the chance of bridging a large number of particles. Figures 5 and 6 show that the settling performance of Chito-cat-2 was better than that of the polymers used.

#### Jar test

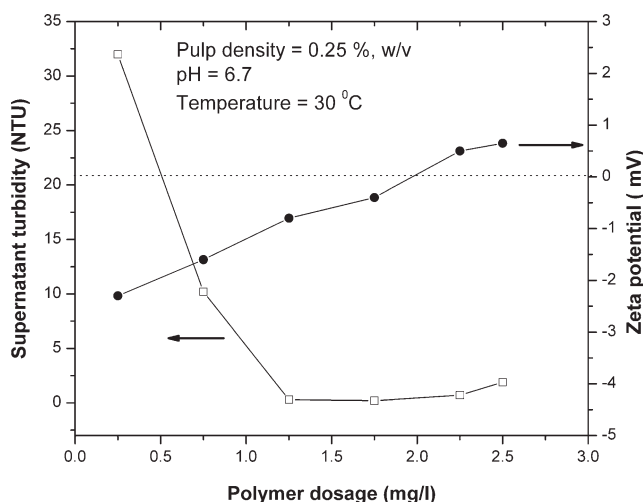
In this experiment, residual turbidity of the supernatant water after mixing and settling was observed with various polymer dosages. The turbidity-removal efficiency of the polymer samples in kaolin suspensions (0.25% w/v) is described in Figure 7.



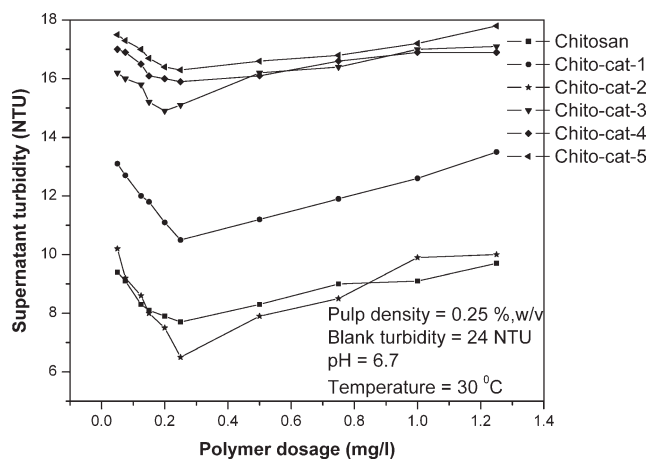
**Figure 7** Turbidity of kaolin suspensions with different polymers and dosages.

An increase in the polymer dosage caused a decrease in the residual turbidity of the supernatant water. This suggests that both the virgin chitosan and the modified chitosan acted as potential water-clarifying agents for kaolin suspensions. We also observed that with the addition of the polymer, the residual turbidity decreased and reached its lowest value around the polymer dosage of 1.75 mg/L. After that, further addition of the polymer increased the residual turbidity value. To investigate this effect, the change in the  $\zeta$  potential of the kaolin particles with different dosages of Chito-cat-2 was measured, and the results are presented in Figure 8. As expected, the negative  $\zeta$  potential value of the kaolin particles decreased with an increase in the polymer dosage, and after an optimal value was reached, further addition of the polymer produced a reversal of charge. Domard et al.<sup>26</sup> also observed this phenomenon and suggested that the progressive addition of the cationic polymer gradually decreases the net negative charge on the kaolin surface, and after a particular dosage, further addition of the cationic polymer reverses the net charge on the kaolin surface. The positively charged kaolin particles then restabilize the suspension. We also observed that the detrimental effect of overdosing was more prominent with a low-molecular-weight polymer (Chito-cat-1), which was less effective in polymer bridging formation. This indicates that both charge neutralization and polymer bridging play important roles in turbidity removal.

Figure 9 shows the jar test results for the iron-ore suspension (0.25% w/v). The optimum value of turbidity was observed at a polymer dosage of nearly 0.25 mg/L. Further addition of the polymer increased the turbidity because of the restabilization of the suspension. Among the polymer samples,



**Figure 8** Effect of the polymer dosage on the turbidity and  $\zeta$  potential of kaolin suspensions.



**Figure 9** Turbidity of iron-ore suspensions with different polymers and dosages.

Chito-cat-2 showed higher turbidity-removal efficiency in an iron-ore suspension.

## CONCLUSIONS

On the basis of these investigations, we conclude that chitosan itself is a good natural flocculating agent, and by the incorporation of the CHPTAC moiety onto chitosan, a modified chitosan can be prepared. The incorporation of CHPTAC has been proved by different physicochemical characterization techniques. We observed that not all the modified chitosans had superior flocculation performance versus native chitosan. Among the modified chitosans, Chito-cat-2 showed the best flocculation performance in both model colloidal suspensions. The flocculation studies lead us to the conclusion that both the polymer bridging and charge neutralization mechanism made significant contributions to the flocculation performance of the polymer samples.

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