

Coagulation–Flocculation of Colloidal Suspensions of Kaolinite, Bentonite, and Alumina by Chitosan Sulfate

Nely Rios-Donato,¹ Ricardo Navarro,² Mario Avila-Rodriguez,² Eduardo Mendizábal¹

¹Centro Universitario de Ciencias Exactas e Ingeniería, Universidad de Guadalajara, Marcelino García Barragán 145, Colonia Olímpica Guadalajara, Jalisco, C.P. 44420, México

²Departamento de Química, Universidad de Guanajuato, Cerro de la Venada, s/n, Colonia Pueblito de Rocha, Guanajuato, Gto. C.P. 36040, México

Received 20 October 2010; accepted 14 April 2011

DOI 10.1002/app.34686

Published online 22 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This article reports on the removal of colloidal suspensions of kaolinite, bentonite, and alumina using chitosan sulfate (ChS). ChS was synthesized by partial introduction of sulfate groups in the chitosan (Ch) structure. The polyampholyte (chitosan sulfate) shows variable charge depending on the pH of the solution. ChS was characterized by FTIR, ¹³C-NMR, elemental analysis, and potentiometric titrations. The ChS coagulation–flocculation capacity for kaolinite, bentonite, and alumina aqueous suspensions was systematically studied. The coagulation–flocculation process was carried out at various

pH values and ChS concentrations. The pH range in which the largest ChS removal capacity was observed depended on particle type (4.5–5.5 for kaolinite, 4.5–7.0 for bentonite, and 7.0–8.0 for alumina). The removal of colloidal particles is explained by charge neutralization due to electrostatic interactions between ChS and particles and particle entrapping when the polyelectrolyte precipitates. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2003–2010, 2012

Key words: chitosan sulfate; flocculation; colloidal suspensions

INTRODUCTION

The removal of turbidity from aqueous effluents before discharging into rivers or lakes is a challenge for water treatment plants. Aluminum salts are frequently used as coagulants of suspended particles. However, these salts can damage the environment since large sludge volumes are produced during the coagulation–flocculation process. Moreover, the presence of aluminum in water in significant quantities has been associated with Alzheimer's disease¹ (>50 mg L⁻¹). Therefore, it is necessary to find more efficient and environmentally safe flocculants for the removal of turbidity from these effluents.

In the search for better flocculants, chitosan (Ch) has been used as a cationic flocculant for particle removal from water.^{2–6} Ch is a linear cationic polymer of high molecular weight, is readily soluble in acidic solutions, and is biodegradable and nontoxic. For example, Khorri⁷ reported that Ch was an effective

agent for the coagulation of suspended solids present in various food processing wastes. Divakaran and Sivansakara Pillai⁸ studied the efficiency of Ch for removing kaolinite particles as a function of pH (covering the range of 5.0–9.0) with an initial turbidity of 10–160 nefelometric turbidity units (NTU). They found that the optimum Ch concentration was 1.0 mg L⁻¹ and the optimum pH was 7.5. Roussy et al.⁹ reported that when using with small amounts of Ch (from 0.42 to 3.33 ppm), almost all of the bentonite particles were removed at fast settling rates in the form of large and stable flocks in the pH range of 5.0–9.0; they proposed a dual removal mechanism by which Ch removed the bentonite particles: (a) coagulation by charge neutralization and (b) flocculation of mineral colloidal particles trapped in the polymer Ch network.

To modify the properties of Ch, various chemical groups can be incorporated in the Ch network. The maximum degree of substitution of Ch (degree of substitution = 3.0) occurs when the functional groups in C₂ (-NH₂), C₃ and C₆ (-OH) are replaced. To obtain a substitute for the natural anticoagulant heparin, Ch was treated with chlorosulfonic acid in pyridine or in dimethylformamide and a water-soluble chitosan sulfate (ChS) with a high degree of substitution of the hydroxyl and sulfate groups was obtained.^{10–16} Wolfrom and Shen Han¹¹ reported the sulfation of the Ch using pyridine and chlorosulfonic acid, where they obtained one sulfoamino group and one sulfate acid ester group per monomer

Correspondence to: Eduardo Mendizábal (lalomendizabal@hotmail.com).

Contract grant sponsor: CONACYT; contract grant number: 44768-Q.

Contract grant sponsor: Fondo Mixto de Fomento a la Investigación Científica y Tecnológica CONACYT-Gobierno del Estado de Guanajuato; contract grant number: GTO-2003-C02-11881.

unit, this compound had good anticoagulant activity. Gamzazade et al.¹⁰ studied how reaction conditions affect the position and degree of sulfation and obtained chitosan sulfates di- and trisubstituted; however the groups at C2 and C3 have only a small amount of sulfation. Naggi et al.¹³ obtained chitosan 6-sulfate by using a 2 : 1 mixture of sulfuric and chlorosulfonic acids. Vongchan et al.¹² prepared under semiheterogeneous conditions sulfated Ch with a degree of substitution of 2.13, which showed strong anticoagulant activity. ChS with low molecular weight (M_v 9000–35,000 Da) and degree of substitution of 1.10–1.63 showed a regular anticoagulant activity.¹⁵ Quan-Li et al.¹⁶ used Collagen and sulfated chitosan (SCS) to coat titanium using a layer-by-layer self-assembly technique. The multilayer processed surfaces displayed reduced platelet adhesion and activation, and prolonged clotting time of activated partial thromboplastin time (APTT) and prothrombin time (PT) compared with untreated titanium.

The aim of the present study was to obtain a new flocculent by partial substitution of the OH groups of the Ch by sulfate groups. The introduction of sulfate groups in Ch makes the ChS a polyampholyte. The ampholytic character of the polyelectrolyte can contribute to reinforcing the electrostatic interactions between chains, favoring the flocculation process. In spite of its interesting properties, ChS has not been studied for the removal of colloidal particles from water. Due to its ampholytic nature this polyelectrolyte can be used to eliminate cationic and anionic colloidal particles from water. The capacity of the ChS for the removal of kaolinite, bentonite, and alumina from aqueous suspensions was evaluated as a function of pH and ChS concentration.

EXPERIMENTAL

Chitosan pretreatment

Ch was pretreated to expand its structure to facilitate the sulfonation reaction. About 1.0 g of dry chitosan (France chitine, France; deacetylation degree, 0.85; average molecular weight, 125 kDa) was dissolved in an aqueous acetic acid solution (1%), and then precipitated by adding 50 mL of a 0.25 mol L⁻¹ NaOH aqueous solution. The suspension was filtered and washed with water until neutral pH was reached. To eliminate possible trapped water within the Ch structure the precipitate was immersed in methanol and stirred for 30 min. Methanol was eliminated by decantation. The precipitate was filtered, washed with methanol, and then immersed in dimethyl formamide (DMF) (Sigma-Aldrich, St. Louis, MO) and agitated for another 30 min. The DMF was removed by decantation and the procedure was repeated to completely remove the methanol. The precipitate was maintained in DMF.

Synthesis of chitosan sulfate

While maintaining the temperature at 0°C, chlorosulfonic acid was added drop wise to DMF to form a complex (HCISO₃-DMF).^{10–12,17} Then, the complex was dissolved in toluene, and the pretreated Ch was added to the toluene solution and stirred for 2 h at room temperature. The precipitate was separated by filtration, washed with a small amount of methanol, and redissolved in NaOH aqueous solution (pH 12.0). It was then purified by ultrafiltration using a polysulphone ultrafiltration membrane (Millipore, 10 kDa) in a Millipore cell (Series 800 Stirred Amicon cell). Then, the remaining water was evaporated and the product dried at 45°C. The dry sulfated product (ChS) was ground and used for further characterization. FTIR spectra were obtained by the pellet technique using KBr (Perkin-Elmer Model Spectrum 100 FTIR spectrometer). The ¹³C-NMR spectrum of the ChS was obtained using a Varian model Gemini 2000, 300 MHz. Elemental analysis was carried out in an Elemental Analyzer Fisons Model EA 1108.

Potentiometric titration curves were obtained using a procedure similar to that described by Parada et al.¹⁸ The Ch and the ChS (0.20 g) were dissolved in 100 mL of previously acidified water (with 0.1M HCl, pH 2.0), and then titrated with a 0.1M NaOH aqueous solution (Metrohn, Tritino model 716 DMS) using a glass electrode and Ag/AgCl as the reference electrode.

Colloidal suspensions

The colloidal particle suspensions of kaolinite (1.0 g L⁻¹, Burgess 17, Burgess Pigment Company, Sandersville, GA), bentonite (5.0 g L⁻¹, Riedel-de-Haën Steinheim, Germany), and alumina (1.0 g L⁻¹, aluminum oxide, Degussa, Germany), were prepared by suspending the particles in 0.01 mol L⁻¹ NaCl aqueous solutions. While agitating, the pH of the suspension was adjusted to the desired value using a HCl aqueous solution (0.1 mol L⁻¹) or a NaOH aqueous solution (0.1 mol L⁻¹). The suspension was allowed to sediment for 2 h, the settled particles were separated by decantation and the resulting suspension was used for the coagulation–flocculation studies.

Zeta potential measurements

To determine the Zeta potential the suspensions were prepared as follows: for the blank, an aqueous solution with an ionic strength equal to that used in the coagulation–flocculation tests (0.01 mol L⁻¹ NaCl) was prepared. Suspensions containing more than 1% of particles were prepared and their ionic strength was adjusted by adding NaCl. The pH was adjusted to pH 11 with 0.1 mol L⁻¹ NaOH aqueous

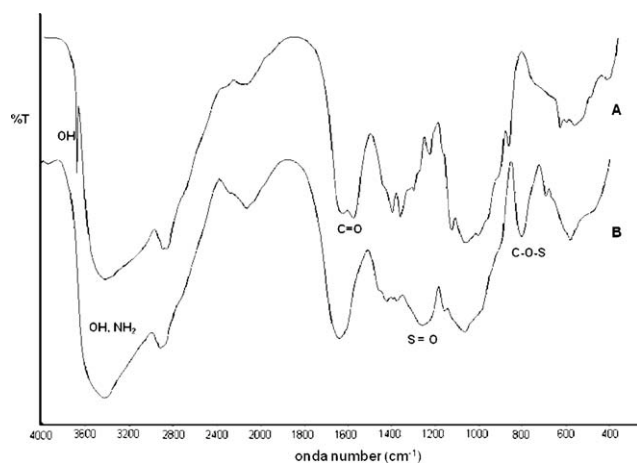


Figure 1 FTIR spectra of: (A) chitosan, (B) chitosan sulfate.

solutions. Then, the suspension was allowed to settle for 2 h and was separated from the settled particles by decantation. The Zeta potential was determined using an Acoustosizer IIS s/m Flow-through System model titrating the suspension with 0.1 mol L⁻¹ NaOH or HCl aqueous solution.

Jar tests

A conventional jar test apparatus (Phipps and Bird model PB-700) was used for the coagulation–flocculation experiments. Colloidal suspensions were adjusted to the desired pH, and 1-L aliquots of the colloidal suspensions were poured into the 2-L jars. A sample was collected to measure initial turbidity (NTU). Next, the desired volume of ChS solution (1.0 mg ChS mL⁻¹) was added to each jar and mixed thoroughly by stirring rapidly for 3 min at 200 rpm. Stirring was maintained for 30 min at a steady rate of 30 rpm. When the stirring was stopped, samples (3 mL) were collected (2.5 cm below surface) to measure the turbidity of the solution as a function of settling time. Suspension turbidities were determined with a UV–visible spectrophotometer (Cary-50 Probe, Varian) measuring absorbance at 350 nm and using a calibration curve obtained with formazine standard suspensions. A blank experiment was systematically performed in the absence of ChS to evaluate the natural decantation process of the suspension under the selected experimental conditions (pH and concentration of suspended material). The results were plotted as a function of sedimentation time, pH, and polyelectrolyte concentration.

RESULTS AND DISCUSSION

Synthesis

The synthesized ChS was an amber solid that was soluble in acid and alkaline aqueous solutions, with

an insolubility window between pH 5.0 and 8.0. Figure 1 shows the FTIR spectra of the ChS in which one can observe the characteristic sulfate stretching vibrations of C—O—S (810 cm⁻¹) and S=O (1240 cm⁻¹).

By comparing the ¹³C-NMR spectra of the Ch [Fig. 2(A)] and ChS [Fig. 2(B)], a displacement of the C₆ signal can be seen from 68 to 60 ppm, due to the substitution of the OH groups for the sulfate groups. The ¹³C-NMR ChS spectra do not show evidence that the sulfate has substituted the hydroxyl group of the C₃, or the amino group in C₂. By using the sulfur and nitrogen atomic ratio S/N, obtained from elemental analysis it was determined that 61% of the OH groups were replaced by sulfate groups (degree of sulfate substitution = 0.61).

ChS is constituted by three types of monomeric units [Fig. 3(A)]; the first (represented by RAC) corresponds to the units containing acetamide groups, the second unit (represented by RH⁺) corresponds to the deacetylated monomeric units that are not sulfated, and the third unit (represented by RSH) corresponds to the deacetylated monomeric units that were sulfated. The molar fractions of RAC, RH⁺, and RSH were determined by titration and their values are represented by *x*, *y* and *z*, respectively, [Fig. 3(A)]

Titration of ChS [Fig. 3(B)] shows three equivalent points (*V*₁ = 2.07 mL; *V*₂ = 4.47 mL; *V*₃ = 9.36 mL).

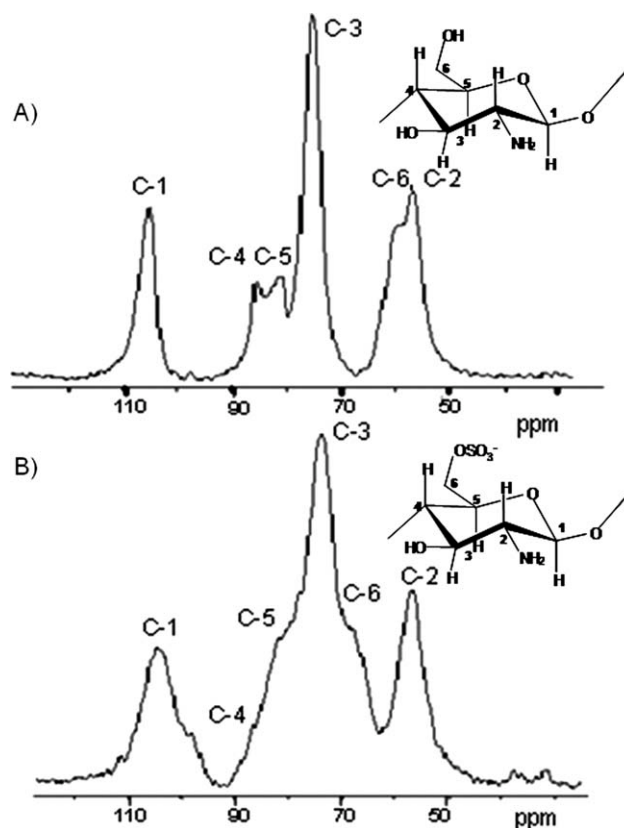


Figure 2 ¹³C-NMR spectra of: (A) chitosan, (B) chitosan sulfate.

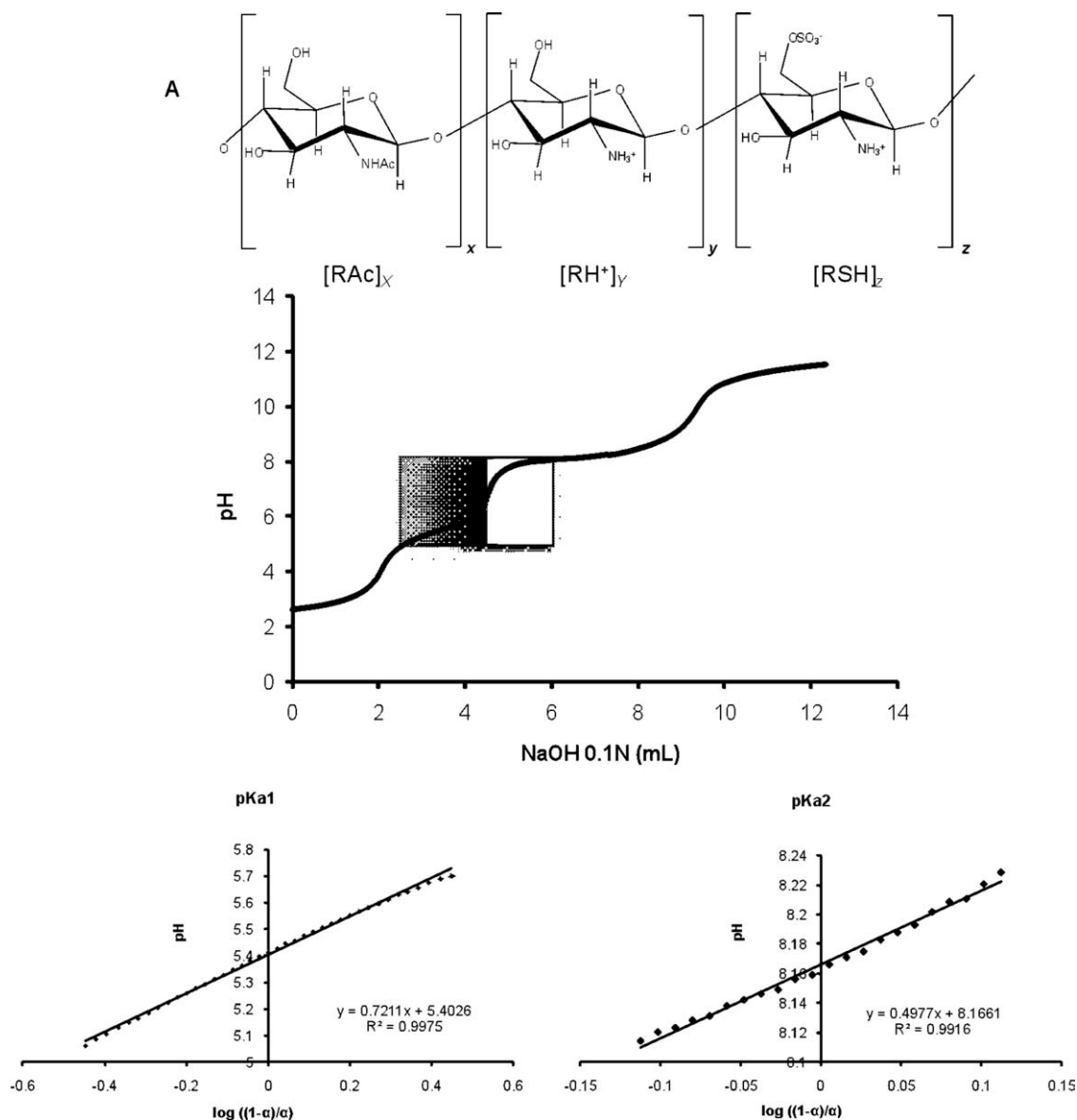


Figure 3 A: Structures of the monomeric units of ChS. B: Potentiometric titration of ChS. 0.182 g of ChS. Titrant: NaOH 0.1 N. C: Determination of pKa values.

The zone before the first equivalent point (V_1) is associated with the neutralization of the excess HCl. The zone between the first equivalent point (V_1) and the second equivalent point (V_2) corresponds to the neutralization of the amine groups (RH^+) of the non-sulfated units of the ChS. The region between the second equivalent point (V_2) and the third equivalent point (V_3) corresponds to the neutralization of the amine groups (RSH) of the sulfated units.

The pK_a was calculated using the Henderson–Hasselbalch equation¹⁶:

$$\text{pH} = \text{pK}_{ai} + \log\left(\frac{1-\alpha}{\alpha}\right) \quad (1)$$

where pK_{ai} is the average pK_{ai} of i ; and α is the dissociation coefficient ($\alpha = (V - V_1)/(V_2 - V_1)$).

The pK_{ai} values were 5.40 and 8.16 for RH^+ and RSH, respectively, [Fig. 3(C)]. The molar fraction of the amino groups of the nonsulfated groups (RH^+) was 0.28 and that of the amino groups of the sulfated units (RSH) was 0.57; this last value is similar to the fraction of sulfated groups obtained by elemental analysis and it was taken as the real degree of sulfation, because the sum of the molar fractions of RH^+ and RSH is 0.85, a value that is similar to the degree of deacetylation reported by the Ch supplier. This result indicates that the amine groups were not modified by the sulfonation reaction.

Zeta potential measurements

Figure 4 shows the Zeta potential as a function of pH for kaolinite, bentonite, and alumina where it

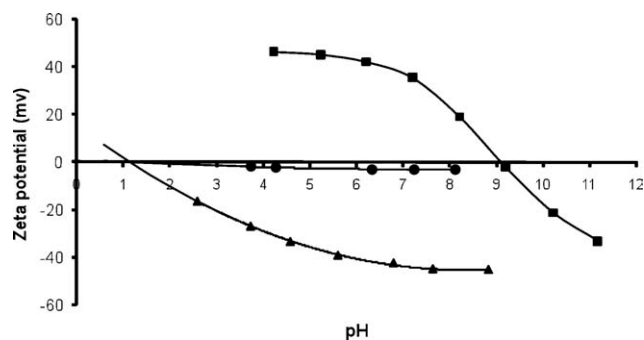


Figure 4 Zeta potential as a function of pH of: kaolinite (▲), bentonite (●), and alumina (◆).

can be observed that the isoelectric points of kaolinite, bentonite, and alumina are 1.2, 0.9, and 9.1, respectively.

Coagulation–flocculation

In Figure 5, the turbidity of kaolinite suspensions as a function of settling time is compared at different pH values and ChS concentrations. At pH 3.0, when ChS

was added, the suspensions had a slightly higher turbidity than the blank, indicating a stabilization effect. When bentonite and ChS interact at this pH, the result is a net high positive charge, and instead of coagulation, the particles are stabilized. At pH 4.5 and 5.0, the combination of an increase in the Zeta potential of kaolinite and a decrease in the net charge of the ChS causes a rapid and very effective coagulation–flocculation (very low turbidity). At pH 5.5, although the fraction of ionized groups is small (around 0.10), because the Zeta potential of kaolinite is high, more kaolinite is removed as the ChS concentration increases. Particle removal can also be helped by ChS precipitation. At pH 6.0 the ChS charge is still positive but too small to be able to coagulate–flocculate the kaolinite particles. At pH values above 6.9, the ChS charge becomes negative and electrostatic attractions between ChS and kaolinite are not possible, and therefore the coagulation–flocculation process does not occur.

When using ChS in bentonite suspensions the following behavior was observed. At pH 3.0, as a result of the low Zeta potential of bentonite combined with

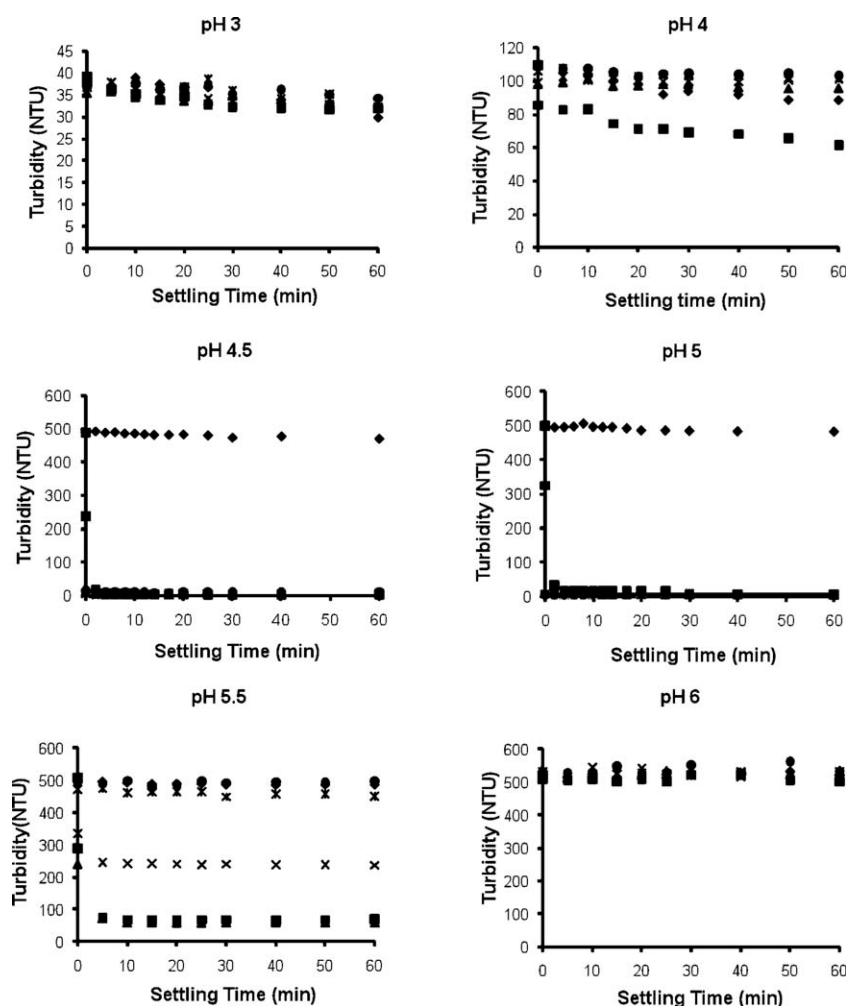


Figure 5 Settling curves for kaolinite suspensions (1 g L^{-1}) at different pH values and ChS concentrations: blank (●); 2 ppm (■), 4 ppm (▲), 6 ppm (×), 8 ppm (*), 10 ppm (●).

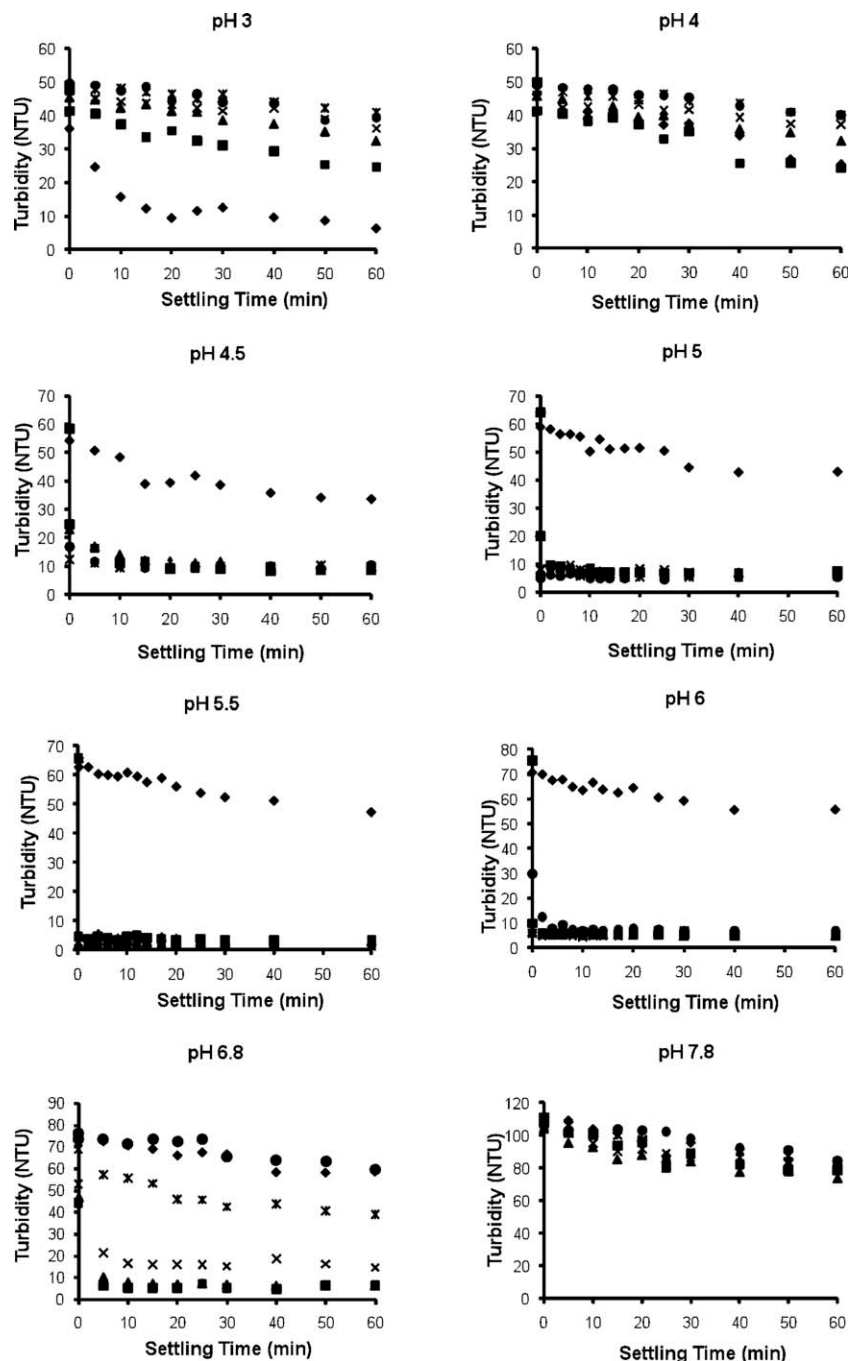


Figure 6 Settling curves for bentonite suspensions (5 g L^{-1}) at different pH values and ChS concentrations: blank (●); 2 ppm (■), 4 ppm (▲), 6 ppm (×), 8 ppm (*), 10 ppm (○).

the amount of ChS added when bentonite and the polyelectrolyte interact the result is a net high positive charge, and instead of coagulation, the particles are stabilized (Fig. 6). When pH increases, ChS charge decreases and for this reason at pH 4.0, at the lower ChS concentrations, the stabilization effect disappears and some coagulation–floculation occurs. As pH increases further, the coagulation–floculation process becomes more efficient due to charge neutralization and is accomplished at faster rates. At pH 4.5–6.0, almost all of the bentonite is

instantaneously settled at all tested ChS concentrations. If pH is increased above 6.0, again there is an imbalance of charges, which causes coagulation–floculation to become less efficient. At pH 6.8, the fraction of negatively charged units of ChS is very small and only at high ChS concentrations is possible to obtain bentonite charge neutralization and thus cause coagulation–floculation. Removal of bentonite can also be aided by bentonite trapping when the ChS precipitates (Fig. 3). At the highest pH value studied (7.8), the ChS charge is negative, and, since

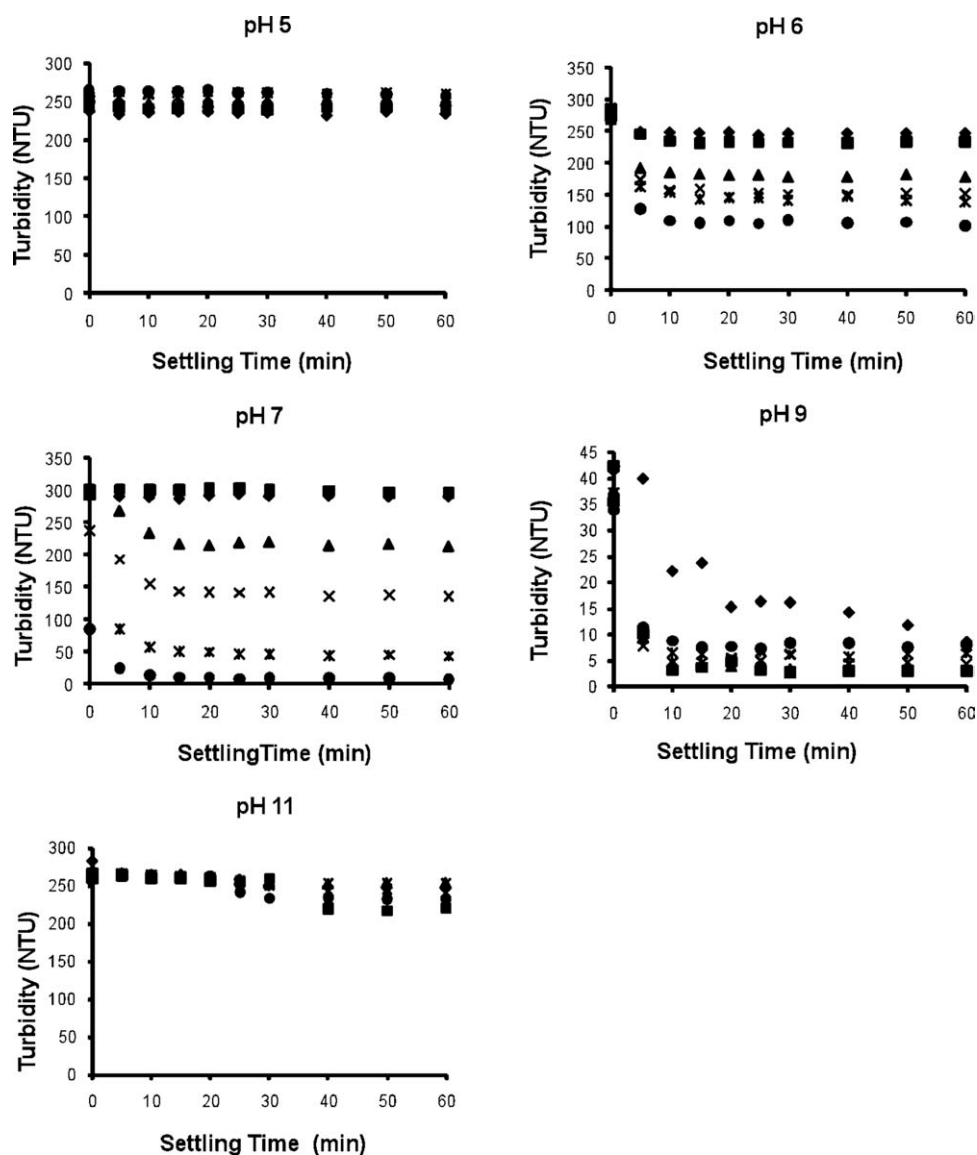


Figure 7 Settling curves for alumina suspensions (1 g L^{-1}) at different pH values and ChS concentrations: blank (●); 2 ppm (■), 4 ppm (▲), 6 ppm (×), 8 ppm (*), 10 ppm (○).

the charge of the bentonite is also negative electrostatic attractions do not occur, making coagulation–flocculation impossible.

ChS was also tested with alumina suspensions (Fig. 7). At pH values lower than 6.8, ChS is in its cationic form (Fig. 3) and because the alumina particles also have a large and positive Zeta potential (+40 mV) the polyelectrolyte is not effective for the removal of alumina. The low removal effect at pH 6.0 can be explained by alumina being trapped when the polyelectrolyte precipitates; at this pH the amount of alumina removed increases as the amount of ChS is increased, which supports the hypothesis that alumina is trapped as the ChS precipitates. At pH values above 6.8, ChS becomes negatively charged and can interact electrostatically with the positively charged alumina particles (Fig. 4), and therefore at a pH of 7.0, by increasing the amount of

ChS, a larger increase in coagulation–flocculation is observed. At pH 9.0, the ChS has a negative charge and the alumina Zeta potential is positive but small (Fig. 4), and thus only a fraction of the ChS added is used for neutralization and the rest causes the alumina to become negatively charged. This explains the partial removal and that less particles are removed as the amount of ChS increases. At pH values above 9.0, both the alumina particles and ChS are negatively charged and particle removal is negligible.

CONCLUSIONS

A ChS was synthesized with a degree of sulfation of 0.57. This polyelectrolyte was water soluble at acidic and alkaline pH with an insolubility window

between pH 5.0 and 8.0. The ChS proved to be effective for the elimination of colloidal particles of kaolinite, bentonite, and alumina. The pH range in which particle removal was achieved depends on particle type (4.5–5.5 for kaolinite, 4.5–7.0 for bentonite, and 6.0–9.0 for alumina). For cationic particles at optimum pH, even at the lowest ChS concentration studied (2 mg L^{-1}), particle removal was very fast and practically all of the colloidal particles were removed. Colloidal particle removal is explained by charge neutralization due to electrostatic interactions between ChS and the particles, and by particle entrapping when the polyelectrolyte precipitates. Cationic and anionic colloidal particles can be removed by ChS because of its ampholytic character.

References

1. McLachlan, D. R. C. *Environmetrics* 1995, 6, 223.
2. Chen, L.; Chen, D.; Wu, C. *J Polym Environ* 2003, 11, 87.
3. Divakaran, R.; Sivasankara Pillai, V. N. *Water Res* 2001, 35, 3904.
4. Dutta, P. K.; Ravikumar, M. N.; Dutta, J. J.; *Macromol Sci Polym Rev* 2002, C-42, 307.
5. Vikhoreva, G.; Bannikova, G.; Stolbushkina, P.; Panov, A.; Drozd, N.; MAkarov, V.; Varlamov, V.; Galbraikh, L. *Carbohydr Polym* 2005, 62, 327.
6. Zeng, D.; Wu, J.; Kennedy, J. F. *Carbohydr Polym* 2008, 71, 135.
7. Khorr, E. *Chitin Fulfilling a Biomaterials Promise*; Elsevier: Department of Chemistry, Republic of Singapore, 2001; p 87.
8. Divakaran, R.; Sivasankara Pillai, V. N. *Water Res* 2002, 36, 2414.
9. Roussy, J.; Van Vooren, M.; Dempsey, B.A.; Guibal, E. *Water Res* 2005, 39, 3247.
10. Gamzazade, A.; Sklyar, A.; Nasibov, S.; Suchkov, I.; Shashkov, A.; Knirel, Y. *Carbohydr Res* 1997, 34, 113.
11. Wolfson, M. L.; Shen Han, T. M. *J Am Chem Soc* 1958, 81, 1764.
12. Vongchan, P., Sajomansang, W., Subyen, D., Kongtawelert, P. *Carbohydr Res* 2002, 337, 1239.
13. Naggi, A. M.; Torri, G.; Compagnoni, T.; Casu, B. In *Chitin in Nature and Technology*; Muzzarelli, R. A. A., Jeuniaux, C., Gooday, G. W., Eds.; Plenum Press: New York, 1986; p 371.
14. Huang, R.; Du, Y.; Yang, J.; Fan, L. *Carbohydr Res* 2003, 338, 483.
15. Vikhoreva, G.; Bannikova, G.; Stolbushkina, P.; Panov, A.; Drozd, N.; Makarov, V.; Varlamov, V.; Galbraikh, L. *Carbohydr Polym* 2005, 62, 327.
16. Quan-Li, L.; Huang, N.; Chen, J. L.; Guojiang, W.; Ansa Z.; Junyning C.; Jin W.; Ping, Y.; Yongxiang, L. *J Biomed Mater Res A* 2009, 89, 575.
17. Hayashi, J. U.S. Pat. 5,229,504 (1993).
18. Parada, L. G.; Crespín, G. D.; Miranda, R.; Katime, I. *Revista Iberoamericana de Polímeros* 2004, 5, 1.