

Flocculation Properties and Adsorption Kinetics of Cationic Starches in Kaolin Suspensions

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ABSTRACT: The flocculation characteristics of cationic starches with degree of substitution (DS 0.32–0.63) have been evaluated in 1.0 wt % kaolin suspension by spectrophotometry and colloid titration. Cationic starch is found to be an effective flocculant for removal of anionic suspension particles. Changes in the electrokinetics of kaolin as a function of pH were investigated in the absence of flocculant. The results show that kaolin in water exhibits a negative surface charge at pH > 2.5. The negative hydrophilic surface sites of kaolin are responsible for the adsorption of cationic starch molecules. The experimental

data of the adsorption of cationic starch (DS 0.51) follow a Langmuir isotherm with maximum adsorption capacities of 16.89 mg/g. For the adsorption of cationic starch, chemical reaction seems significant in the rate-controlling step and the pseudosecond-order chemical reaction kinetics provides the best correlation for the experimental data. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2841–2849, 2007

Key words: cationic starch; kaolin; flocculation; adsorption; kinetics; isotherms

INTRODUCTION

Flocculation processes facilitate the removal of suspended solids and colloids. The addition of synthetic polymeric, inorganic salts or surfactants causes the agglomeration of these particles, allowing their elimination by settling or filtration. Water-soluble synthetic polymers^{1–4} are common additives for controlling stability as well as rate of sedimentation of flocculating suspensions. Synthetic polymeric flocculants such as polyacrylamide,¹ poly(acrylic acid),² poly(diallyl dimethyl ammonium chloride),³ poly(styrene sulfonic acid),⁴ etc. have been developed over the last 30 years to meet the needs of wastewater treatment, mineral processing, and paper drainage and retention during manufacture. In spite of their effective as flocculating agents, a potential problem associated with their use is the lack of biodegradability and high operation cost. In this respect, development of substitutes based on natural polysaccharides and their derivatives containing required functional groups can be more attractive from the biodegradability point of view, and an important factor here will be matching the performance.

Of all these nature polysaccharides, starch appears to be a very fascinating field for research with high possibilities for wastewater treatment, thereby enlarging the range of its utilization. There are several types

of starch derivative flocculants currently investigated in water treatment. Cationic starches, especially those with high DS, are the most common type of starch derivative flocculants investigated due to the efficient flocculation of anionic trash and produce a good settling performance for relatively low cost. Over the recent years many studies have been performed to examine flocculation behavior and to elucidate the interaction between cationic starch and substrate.^{5–15} All authors reiterated the point that the adsorption and flocculation processes must occur simultaneously to work and should not be thought of as separate mechanisms.

Björklund et al.,⁵ Bratskaya et al.,⁶ Jäinström et al.,⁷ and Sableviciene et al.⁹ have observed the importance of solid loadings upon polymer adsorption. The studies concluded that the final adsorption capacities are controlled by the amount of available surface area in the system. Nyström et al.⁸ investigated the interactions between highly cationic starch and likewise cationic calcite and have concluded that the flocculation is dependent on the adsorption and is in most cases enhanced with increased adsorption. Jäinström et al.⁷ examined the effect of solid loadings upon floc strength and stated that the solid loadings can affect floc strength and hence control the rate of floc breakup under the influence of shear. Gray and Ritchie¹⁶ also examined the effect of polyelectrolyte properties upon floc strength and hence rate of floc breakup and concluded that floc strength increases with adsorption capacity of polyelectrolyte on oppositely charged substrate.

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TABLE I
The Characteristics of Cationic Starch

Flocculants	Nitrogen (%)	DS	Intrinsic viscosity (dL/g)	Apparent charge density (mmol/g)
CS1	2.07	0.32	3.47	1.309
CS2	2.42	0.40	4.95	1.728
CS3	2.89	0.51	8.26	2.127
CS4	3.25	0.63	6.38	2.441

Although the past works indicated cationic starch with high degree of substitution could be effective flocculants for wastewater treatment, there has been very little work undertaken examining adsorption kinetics of cationic starch on kaolin in detail. In previous studies of flocculated systems it has either been observed or assumed that the adsorption process is complete within a several-second period; however, our work shows that adsorption kinetics are not always so simple.

In this study, the flocculation in kaolin suspension with cationic starches was first investigated by manipulating a number of variables such as pH, ionic strength, cationic starch concentration, and temperature. And then adsorption kinetics and adsorption isotherms were investigated.

EXPERIMENTAL

Materials

Corn starch (industrial grade) was purchased from Dacheng Corn starch (Jilin, China). 2,3-epoxypropyltrimethylammonium chloride was provided by Qionglai Starch Company. Sodium hydroxide and other chemicals used in this study were of analytical grade.

A kaolin sample was procured from Xinong Chemical. The physical and chemical characteristics of the material (data provided by the manufacturer) are as follows: The kaolin particles have an average spherical diameter of 2.0 μm (> 88% w/w); the specific surface area measured by BET method was 10.62 m^2/g ; density of kaolin: 2.25 g/cm^3 ; moisture: 0.3% maximum; silica: 53% \pm 0.5%; alumina: 44% \pm 0.5%; ferric oxide: 0.5%, titania: 0.2%; and loss on ignition 0.5%.

Synthesis of cationic starches by dry process

Corn starch (25 g) was thoroughly mixed with 3 mL sodium hydroxide aqueous solution (100%, w/v) and 4 mL isopropanol for 15 min using mechanical stirrer. 2,3-epoxypropyltrimethyl-ammonium chloride (either 10, 12, 15, or 18 g) was added to the previous mixture at room temperature and thoroughly mixed for 15 min and transferred to stoppered bottles and kept in thermostated water bath for 3 h at 80°C. At the end

of the reaction time, the reaction mixture was acidified with ethanol containing acetic acid and then was filtered, and washed with ethanol : water mixture (85 : 15) until the filtrate was free from chlorine ion. The products were dried at 40°C. The dried samples were stored in a desiccator at room temperature before use. The characteristics of synthetic products are given in Table I.

Nitrogen content

The extent of amination was traced by determining the nitrogen content (N%) using the semimicro *Kjeldahl* method.¹⁷ N% was determined according to the following equations:

$$\text{N}\% = \frac{1.401 \times c \times (V_1 - V_0)}{m} \times 100 \quad (1)$$

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

The degree of substitution (DS) for cationic starch bearing quaternary ammonium group was calculated from nitrogen content:

$$\text{DS} = \frac{11.57 \times 162(\text{N}\%)}{100 - 13.44(\text{N}\%)} \quad (2)$$

Colloid titration

Polyelectrolyte titration⁶ was used for the analysis of cationic starches with a high charge density. For polyelectrolyte titration of cationic starches, a dilute solution of potassium polyvinylsulfate (KPVS, obtained from Chengdu kenong Chemical) and toluidine blue O (obtained from Beijing Chemical) as an indicator were used. For the assay, 1 mL 0.1 mol/L HCl, 1 mL 0.05% toluidine blue O solutions, and 1 mM NaCl solution were added to the suitable amount of cationic starch solution. The total volume of the solution was 50 mL. During titration with KPVS the solution was stirred with a magnetic stirrer. At the end of titration

the color of solution changed from blue to violet. In the case of polyelectrolyte titration of water-soluble cationic starches the standard deviation was less than 3% of the mean value.

Charge density (ED) (mmol/g) was calculated according to the formula

$$ED = \frac{c \times V}{m} \quad (3)$$

where c is the titrant (KPVS) concentration (mmol/L), V is the equivalent titrant volume; and m is the content of starch in titrated solution (g).

Intrinsic viscosity

Intrinsic viscosity measurements of the cationic starch solutions were carried out with an Ubbelohde viscometer at $25^\circ\text{C} \pm 1^\circ\text{C}$. The measurements were performed with 0.4 wt % solutions of cationic starches. The pH of the aqueous solution is neutral. The intrinsic viscosities were obtained (from the point of intersection) after extrapolation of two plots i.e., η_{sp}/C versus C and $\ln\eta_r/C$ versus C to zero concentration. Where C is the cationic starch concentration (g/dL) and η_{sp}/C is reduced viscosity, calculated from the relation $\eta_{sp}/C = (\eta_0 - \eta)/\eta_0 C = (t - t_0)/t_0 C$. In the expression t is the time of flow of cationic starch solution and t_0 , the time of flow of solvent at the temperature of measurement. $\ln \eta_r/C$ is the inherent viscosity, where η_r is relative viscosity, calculated from the relation $\eta_r = t/t_0$.

Zeta potential measurements

The zeta potential of kaolin at different pH conditions in the absence of cationic starches was determined by a JS94H Minitype Electrophoresis Meter (Shanghai zhongshun Instruments) at 0.01 wt % solids.

Flocculation experiments

The cationic starch derivatives (0.5 g) were dissolved in 100 mL deionized water with stirring for 30 min at 60°C and 24 h at room temperature and 0.5% (w/v) solution were used for flocculation experiments.

Kaolin (2 g) was dispersed in a 250-mL beaker with 150 mL water with and without NaCl additions using ultrasonic treatment for 15 min, followed by vigorous stirring during 1 h. A solution of cationic starch was added in different doses and then water was poured to get exactly 200 mL (the final concentration of kaolin in the dispersion was 1.0 wt %). Immediately 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. A clar-

fied layer of liquid was formed in the upper part of the test tube. At the end of the settling period, the absorbency of the supernatant liquid was measured with a spectrophotometer (Spectrophotometer-722, Shanghai Qinghua Analytical Instruments Factory, China). The experiments were carried out at temperature ($15\text{--}60^\circ\text{C}$). Flocculation efficiency (FE) was calculated according to the formula:

$$FE = \frac{A_0 - A_1}{A_0} \times 100\% \quad (4)$$

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

Adsorption experiments

The adsorption isotherms of water-soluble cationic starches onto kaolin particles were determined by the depletion method. Kaolin (1 g) was suspended in 50 mL of 1 mM NaCl solution at 25°C and stirred for 10 min with a magnetic stirrer. A volume of 50 mL of water-soluble cationic starch solution (of required concentration) was added to the kaolin dispersion and the stirring was extended for predetermined time. During equilibrating the kaolin was settled down and a clarified layer of the liquid was formed. A volume of 50 mL of the formed clarified liquid was removed and analyzed using colloid titration procedure. The amount of adsorbed starch was calculated using the difference between known initial starch concentration and concentration measured in supernatant.

RESULTS AND DISCUSSION

Characteristics of cationic starches

Table I gives the characteristics of various grades of cationic starches (CS) i.e., the series of CS1, CS2, CS3, and CS4 used as flocculant in the present study. From Table I, it is clear that apparent charge density of cationic starches increases as DS of cationic starches increase. Cationic starch derivatives studied were water-soluble and showed high positive zeta potential over broad pH range due to the presence of quaternary ammonium groups, which provides sufficient electrostatic stabilization. Table I also shows that the intrinsic viscosity of cationic starches increase with increasing in DS up to DS = 0.51. However, at higher DS (0.63) the intrinsic viscosity was lower than it could be expected from the correlation. We assume that the decrease in viscosity at higher DS could be attributed to partial cleavage of the glycosidic linkages resulting from increasing in the dosage of sodium hydroxide going with the increase of cationic monomer concentration, and this led to a decrease in molecular weight of starch molecules. The degraded starch was

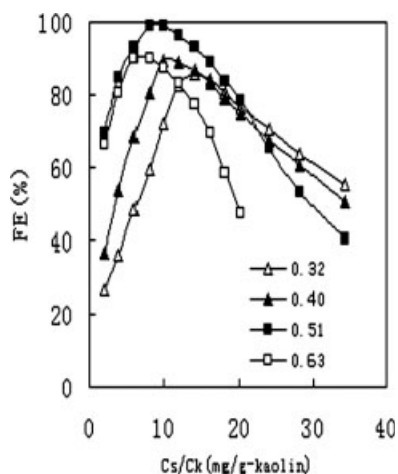


Figure 1 Effect of flocculant dosage on FE (temperature, 25°C; pH 5.0; NaCl, 10 mM).

not resistant to shear and could not maintain the integrity of starch granule and thereby produced a lower intrinsic viscosity.

Effect of flocculant dosage and DS on flocculation

From Figure 1, it can be seen that FE increases with increasing the flocculant dose to reach a maximum value and then decreases. The flocculant dose giving rise to maximum FE value is considered as optimal dose value. The optimal dose values depend on DS of cationic starch derivatives and decrease with increasing DS. The influence of flocculant dosage can be explained because bigger flocs are formed when flocculant dosage increases. The isoelectric point of the kaolin in the present investigation is found to lie in pH 2.5 and is about 0.3 units higher than the reported values.¹⁸ At pH < 2.5, kaolin particles display a net positive zeta potential due to the protonation of the surface of kaolin. At pH > 2.5, kaolin particles display a net negative zeta potential due to the deprotonation of the surface. Adding cationic starches to the kaolin suspension leads to attraction between the suspended particles bearing negative charge and the cationic groups of cationic starches. The cationic starch molecules attached to solid particles still have free active sites that can be adsorbed on the remaining free surface of other particles. This process results in "bridging" between solid particles and in the consequent formation of large flocs having a three-dimensional network structure. Besides bridging, the addition of the flocculants increases charge neutralization to reach zeta potential value of zero at which maximum flocculation occurs. This occurs at the optimal dose value. After this situation, higher flocculant dosage may impart a positive electric charge to the suspended particles high enough to cause mutual repul-

sion. In addition, at higher dosage starches covers most of the available sites on each particle and bridging becomes negligible. The overall result is redispersion of the flocs because of electrostatic repulsion.

FE increases with increasing DS, i.e., the higher DS, the lower amount of starch derivative is required to reach optimal flocculation efficiency (Fig. 1). Figure 1 also shows that further increase of DS did not influence the value of kaolin flocculation, when DS was above 0.51. This can be explained by the fact that at this case electrostatic repulsion between adsorbed macromolecules and macromolecules in the solution increase, thereby reducing the adsorption of cationic starches at kaolin surface.

As shown in Figure 1, highly charged cationic starches showed higher flocculation values at low dosages, whereas cationic starches with lower DS showed high flocculation values at high dosages. Highly charged cationic starches at low dosages adsorb strongly onto the negatively charged kaolin particles by means of electrostatic forces and thus the electrical double layer repulsive forces between them is eliminated to form colloids of flocs. The small flocs that were formed by electrostatic charge patch mechanism settle down in a reasonable rate,¹⁹ but it is assumed that these flocs are in very small size compared to those obtained using long chain cationic starch. The effectiveness of cationic starches decreases with an increase in the dosage, since the negative charges on colloidal particles decrease upon cationic starches adsorption on the surface. It is also assumed that the negative charges become positive at high dosages. It is likely that in the presence of high cationic starches, the strong electrostatic repulsive forces are in effect between cationic starches and positively charged flocs, which prevent the flocculation of kaolin suspension. On the other hand, at relatively high dosages (> 16.14 mg/g, where mg/g represents mg of

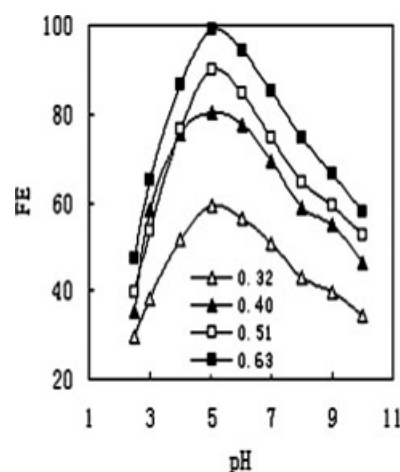


Figure 2 Effect of pH on FE (temperature, 25°C; C_s/C_k , 8.07 mg/g; NaCl, 10 mM).

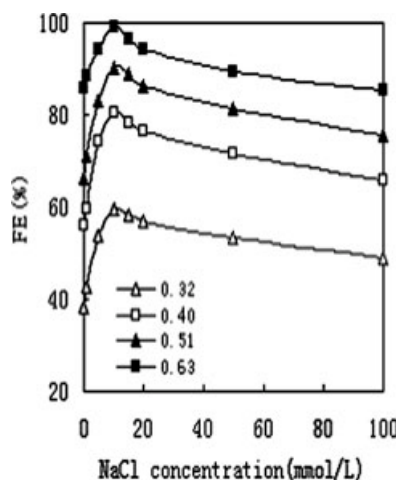


Figure 3 Effect of salt concentration on FE (pH 5.0; temperature, 25 °C; C_s/C_k , 8.07 mg/g).

floculants per g of kaolin), low cationic starches were more effective than the high cationic starches in terms of clarity values.

Effect of pH on flocculation

The suspension pH plays a significant role in flocculation process. Figure 2 demonstrate that FE is pH dependent, and at pH 5.0 FE shows higher values. However, apart from the value, both low and high pHs FE of all cationic starches decrease. The pH in a suspension determines the sign of surface charge of the particles and can change charge characteristics of cationic starch chain and their conformation in solution.²⁰ At acid medium configuration of cationic starches extends due to electrostatic repulsion between the charged groups on cationic starches chain and at low pHs due to adsorption of H^+ ions onto negative charge centers of kaolin leading to their destabilization, which result in the available active sites of kaolin surface decrease. And so flocculation value is lower. The relatively low flocculation values at high pH may be attributed to the weakened electrostatic attraction of the negative particle surface, since Coulomb force between OH^- and cationic starch sample reduces free active sites in cationic starches that can be adsorbed on the surface of kaolin particles. Therefore, electrostatic bond formation between cationic starch and OH^- in the solution may inhibit adsorption of cationic starch onto the external surfaces of negatively charged kaolin particles.

Effect of salt on flocculation

Figure 3 shows that effect of salt concentration on flocculation. Although the adsorption of cationic starches was nearly unaffected by salt concentration, FE in comparison with distilled water was significantly enhanced at all studied ionic strengths. Several researchers also observed

this phenomenon.^{6,7,9,15} As shown in Figure 3, at ionic strengths lower than 10 mM, FE for all cationic starches studied increases gradually by the salt content variation and for salt concentrations higher than 10 mM, the destabilization occurs with less flocculants. Moreover, when the ionic strength increases, the domain of instability becomes larger. The decrease of FE with the ionic strength corresponds to the diminution of interparticle repulsions and the formation of loops and tails. The particular variation at high ionic strengths is related to the conformation of cationic starches with high charge density, which is very sensitive to the ionic strength of the solution. In pure water, cationic starches are completely stretched. After contact with a particle, intramolecular repulsions prevent a complete spreading of cationic starches. Thus positive areas are easily created and aggregation is promoted. Increasing the ionic strength induces the screening of electrostatic repulsions between neighboring charged units and leads to a more flexible conformation. Thus, during adsorption, reconformations occur, chains adopt a flatter conformation on the surface, and the positive regions are smaller. One of the most conspicuous results from the flocculation studies was the discovery of a critical salt concentration in the kaolin suspensions. A certain salt concentration was necessary to compress the thickness of the electrostatic double layer to bring two particles close together. This implies that the thickness of the adsorbed layer is not too large relative to the electrostatic double layer.

Effects of temperature on flocculation

The experimental results clearly show that flocculation of the kaolin suspension is a temperature dependent process for all flocculants tested (Fig. 4). In the working temperature range between 15 and 60 °C, FE shows a considerable increase with temperature to the

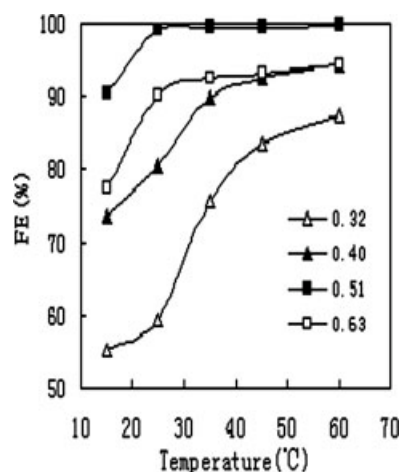


Figure 4 Effect of temperature on flocculation (pH 5.0; NaCl, 10 mM; C_s/C_k , 8.07 mg/g).

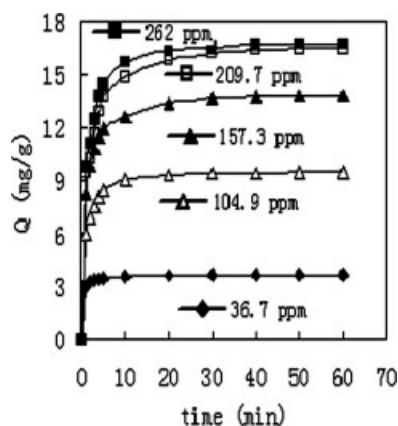


Figure 5 Adsorption of CS3 on kaolin versus time (pH 5.0; temperature 25°C; NaCl concentration, 10 mM).

point of 60°C. Macroscopic observation reveals that flocs become tighter and larger as temperature increases for the cationic starch flocculants. At low temperature the kaolin surface was saturated with adsorbed cationic starch that electrosterically stabilized the particles. When the temperature was raised, the adsorbed starches collapsed onto the kaolin surface and no longer gave steric stabilization. Simultaneously, the cationic starches in solution phase separated to give cationic colloidal particles that heterocoagulated with kaolin. The collapse of a poly(*N*-isopropylacrylamide-*co*-diallyldimethylammonium chloride) steric layer by increasing temperature has been shown to occur with TiO₂ stabilized.²¹

The observed increase in flocculation with temperatures may be of some industrial importance, since it indicates that it is possible to control the structure in the suspension by adjusting the temperature. The observed temperature effects may have several different explanations. A change in the entropy of the system when two particles with adsorbed polymer layers approach each other is a probable explanation (compare the theory about steric stabilization). The flocculation behavior may also depend on the conformation of the starches on the surface and their relaxation times in relation to the particle-particle collision frequency, and this may be strongly affected by temperature changes.

Adsorption kinetics

After cationic starches adsorb on negatively charged particles, they will change their conformation until eventually an equilibrium conformation is reached. Figure 5 shows an example of the kinetics of the adsorption of CS3 (DS 0.51) at pH 5.0. It can be seen that the adsorption time is a strong function of cationic starch coverage on kaolin surface. For low dosage the adsorption time is very short (10 min or shorter), whereas for highly coated surfaces the equilibrium adsorption can

take 30 min or even longer, because lateral interactions prevent polymer flattening. The reformation is likely to be important for cationic starch on kaolin. Since the cationic starch-kaolin interaction is weak, it is possible that adsorbed cationic starches desorb from the kaolin surface as well, resulting in a steady state in which adsorption and desorption are balanced.

Figure 5 shows the kinetics of adsorption for five dosages ranging from 36.7 to 262 ppm. The adsorption amount of flocculants onto kaolin surface at all concentrations increases with time, with the majority of flocculants being adsorbed within 10 min. The flocculants dosage can be split up into three different dosage regimes: (a) low dosage (36.7 ppm), (b) intermediate dosage (104.9–209.7 ppm), and (c) high dosage (262 ppm). At low dosage, all of the flocculants adsorb onto kaolin surface within 10 min. Similarly at high dosage, the flocculants reach adsorption equilibrium with the kaolin surface (16.67 mg/g) within 10 min. However, an unexpected effect is observed for the intermediate dosage, where adsorption continues to occur and the flocculants neither fully adsorb nor reach equilibrium with 10-min experimental time scale, after which time further adsorption occurs. Another interesting observation is that within 262 ppm dosages, the adsorption capacity was lower than it could be expected from the correlation.

Experimental data on adsorption kinetics indicate that the adsorption of cationic starches by kaolin particles is largely determined not by relatively fast diffusion of macromolecules to the surface but rather by secondary processes of redistribution of adsorbed macromolecules. From the present experiment, we observed a fast increase in the degree of flocculation after a contact time of 1–5 min. This means that, during the relatively fast polymer adsorption in a stirred suspension, the collision efficiency increases considerably, boosting the flocculation rate. Subsequently, the rate of the adsorption of cationic starch decreases. No significant change in the adsorption of cationic starch is observed after about 30 min. It is obvious that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between cationic starch adsorbed on the surface of kaolin particle and solution phase. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid, as observed by Solberg and Wågberg for cationic polyacrylamide.¹ Then, a slower adsorption would follow as the available adsorption site gradually decreases and repulsive forces increase.

Pseudofirst-order model

The adsorption of cationic starch onto kaolin may involve chemical adsorption, which can control the

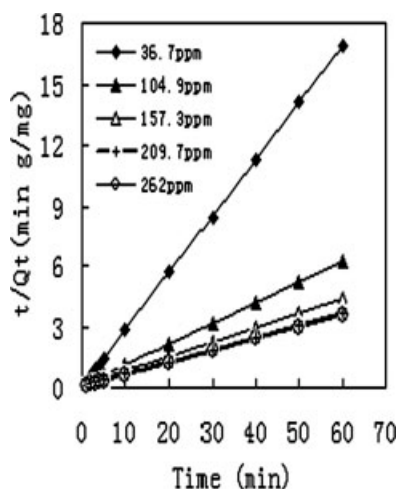


Figure 6 Pseudosecond-order plots for CS3 on kaolin at various initial concentrations (pH 5.0; temperature 25°C; NaCl concentration, 10 mM).

reaction rate. To investigate the mechanism of adsorption and potential rate-controlling steps such as mass transfer and chemical reaction, t the adsorption kinetics can be described by a pseudofirst-order equation or a pseudosecond-order.

The pseudofirst-order model²² can be expressed as

$$\frac{dQ_t}{dt} = -k(Q_t - Q_e) \tag{5}$$

where Q_e and Q_t (mg/g) are the amount of adsorbed cationic starch on the adsorbent at equilibrium and at time t (min), and k is the adsorption constant of first-order sorption (min^{-1}). Equation (5) can be transformed as

$$\ln(Q_e - Q_t) = \ln Q_e - kt \tag{6}$$

When plotted (not shown here) as $\ln(Q_e - Q_t)$ versus t for the adsorption of CS3 at 25°C and at a pH 5.0, the adsorption data do not fit this equation, as the R^2 values for different initial concentration ($C_0 = 36.7, 104.9, 157.3, 209.7,$ and 262 ppm) are found to be 0.8423, 0.9328, 0.5047, 0.95, and 0.8529, respectively. The cal-

culated Q_e values obtained from the first-order kinetic model do not give reasonable values, which are too low compared with experimental Q_e values. This finding suggests that the adsorption of cationic starch on kaolin is not diffusion-controlled and the process does not follow the pseudofirst-order adsorption rate expression. Therefore, any reaction occurring is not likely to be a first-order reaction.

Pseudosecond-order model

A pseudosecond-order model may also describe the kinetics of adsorption. The rate of pseudosecond-order reaction is dependent on the amount of cationic starch adsorbed on the surface of adsorbent and the amount adsorbed at equilibrium. The pseudosecond-order model²³ can be expressed as

$$\frac{dQ_t}{dt} = -k_2(Q_e - Q_t)^2 \tag{7}$$

Integrating eq. (7) for the boundary conditions $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_e$ gives

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{8}$$

where k_2 is the rate constant of the adsorption (g/mg min), Q_e the amount of CS3 adsorbed at equilibrium (mg/g), and Q_t the amount of adsorbed CS3 on the surface of kaolin at any time t (mg/g). $k_2 Q_e^2$ (h) is the initial adsorption rate (mg/g min).

Figure 6 shows the plot of t/Q_t versus t for the adsorption of CS3 on kaolin at different initial concentration. The values of k_2 and Q_e can be obtained from the intercept and the slope of the line, respectively. The results are listed in Table II for each initial concentration. The straight lines for all initial concentrations (Fig. 6) with extremely high correlation coefficients ($R^2 > 0.99$) for pseudosecond-order kinetic models compared to those for pseudofirst-order for the adsorption of CS3 onto kaolin strongly suggest that all the adsorption system are the rate of pseudosecond-order kinetic models, And the experimental Q_e values

TABLE II
Kinetics and Langmuir Parameters for CS3 Adsorption onto Kaolin

Initial conc. (ppm)	Pseudo-second order model					Langmuir		
	Experiment Q_e (mg/g)	Calculated Q_e (mg/g)	k_2 (g/mg min)	h (mg/g min)	R^2	Q_e (mg/g)	b (L/mg)	R_2
36.7	3.55	3.56	2.32	29.40	0.9999	16.89	0.219	0.9966
104.9	9.65	9.80	0.123	11.81	0.9999			
157.3	13.77	14.00	0.0794	15.56	0.9999			
209.7	16.53	16.81	0.0485	13.70	0.9999			
262	16.67	16.89	0.0104	29.67	0.9999			

pH 5.0; temperature 25°C; NaCl concentration, 10 mmol/L.

are in agreement with the calculated ones, which does not happen with the pseudofirst-order kinetic equation. Both facts suggest that the adsorption of cationic starch followed the pseudosecond-order model, which relies on the assumption that chemical adsorption involving valency forces between the hydrophilic edge sites of kaolin and cationic starch may be the rate-limiting step.

From Table II, it is evident that the initial adsorption rate, h , increases with the increase in initial cationic starch concentration, which is in good agreement with the uptake results shown in Figure 5. It is also evident that the value of k_2 decreases as the initial concentration increases, which means that cationic starch adsorption on kaolin is less favorable at high initial concentration. This can be explained by the fact that at this case electrostatic repulsion between adsorbed macromolecules and macromolecules in the solution increase, thereby reducing the adsorption of cationic starch adsorption on kaolin surface. However, excess flocculants have higher values of h and k_2 compared with intermediary dosage. It is also evident from Figure 5 that the adsorption processes for cationic starch is highly dependent on the initial concentration.

Adsorption isotherm

Adsorption isotherms describe how adsorbates interact with adsorbents and are critical in optimizing the use of adsorbents. Therefore, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems. To optimize the design of a sorption system to remove suspension particles from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. The experimental data of equilibrium isotherms for cationic starch was modeled using Langmuir isotherm.

The Langmuir isotherm has been widely used to describe single-solute systems. It is based on the assumption that intermolecular forces decrease rapidly with distance and consequently it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species. Theoretically, the adsorbent has a finite capacity for the adsorbate. Once a cationic starch molecule occupies a site, no further adsorption can take place at that site. Langmuir model^{24,25} is written as

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (9)$$

where C_e presents the equilibrium concentration of cationic starch (ppm) in the solution, Q is adsorbed amount of cationic starch (mg/g), Q_m represents the

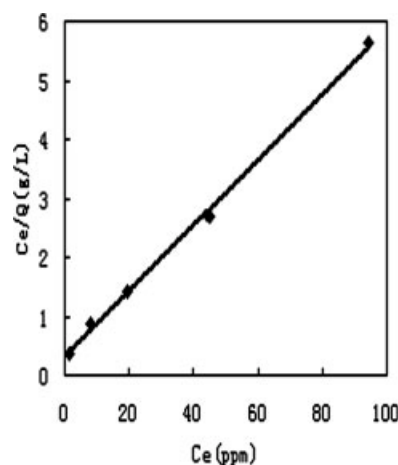


Figure 7 Adsorption isotherm of CS3 (pH 5.0; temperature 25°C; NaCl concentration, 10 mM).

maximum amount of adsorbed cationic starch (mg/g), and b is a constant related to the energy of adsorption (L/mg). The values of Q_m and b were calculated from the slope and the intercept of linear plot of C_e/Q versus C_e (Fig. 7) and presented in Table II.

The isotherm of cationic starch were found to be linear over the whole concentration range and the correlation coefficients (R^2) were extremely high 0.99, suggesting that the adsorption of cationic starch onto kaolin closely follow a Langmuir isotherm. The high fit to the Langmuir model for cationic starch suggests that the adsorption is limited with monolayer coverage and the surface is relatively homogeneous in terms of functional groups.

The effect of isotherm shape can be used to predict whether a sorption system is favorable or unfavorable in batch processes. According to Gupta et al.,²⁶ the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R , which is defined by the relationship:

$$K_R = \frac{1}{1 + bC_0} \quad (10)$$

where K_R is a dimensionless separation factor, C_0 is initial concentration (mg/L), and b is the Langmuir constant (L/mg). The value of K_R indicates the type of the isotherm to be unfavorable ($K_R \geq 1$), linear ($K_R = 1$), favorable ($0 < K_R \leq 1$), or irreversible ($K_R = 0$).

The K_R values calculated indicate that adsorption of CS3 on kaolin is favorable ($0 < K_R \leq 1$) for all initial CS3 concentrations.

CONCLUSIONS

Effective cationic starch-induced flocculation is due to the contributions from several factors representing the

characteristics of the particle surface, cationic starches, and suspension. Some of the factors are more dominant for effecting flocculation under certain conditions. It is possible to judiciously control the flocculant concentration to achieve the desired increase in flocculation efficiency and to optimize DS of cationic starches to leverage the benefits. CS3 (DS 0.51) was found to perform best since it could provide the necessary number of positively charged density and also had the reasonable size to help bridging flocculation under optimum conditions. FE is pH dependent, and at pH 5.0 FE shows higher values. However, apart from the value, both low and high pHs FE of all cationic starches decrease. Addition of electrolyte leads to the surface charge screening and compress the thickness of the electrostatic double layer, which facilitates bringing two particles close together. The maximum flocculation values increased with increase in temperature, which indicates higher temperature facilitates the flocculation.

The adsorption kinetics of CS3 onto kaolin has been investigated as a function of flocculant dosage. Low flocculant dosages achieve complete adsorption and high flocculant dosages achieve an equilibrated adsorbed amount after 10 min. In contrast, the intermediate flocculant dosages display more complex kinetics, which are incomplete over a 30-min period. The equilibrium adsorption data of CS3 can be best modeled using Langmuir model with equilibrium adsorption capacities of 16.89 mg/g. For the adsorption of CS3, chemical reaction seems significant in the rate-controlling step and the pseudosecond-order chemical reaction kinetics provides the best correlation for the experimental data.

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