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A kinetic investigation of cationic starch adsorption and flocculation in kaolin suspension

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Abstract

The flocculation kinetics of kaolin particles suspended in 0.01 mol/L NaCl solution and adsorption properties of cationic starch on kaolin surface have been investigated at pH 5.0. Adsorption kinetics of cationic starch followed pseudo-second-order model ($R^2 > 0.98$). Flocculation kinetics showed that increase in flocculant dosage resulted in higher rate constants for the flocculation process and lower rate constant for the aggregate breakage. The rate of aggregation of particles and frequency of collisions of particles are very slow and the two steps determined the rate of flocculation process. The adsorption of cationic starch on the kaolin surface followed Langmuir isotherm ($R^2 > 0.99$). Thermodynamic study indicated that the values of ΔG^θ were strongly temperature-dependent and that cationic starch adsorption onto kaolin particles entropically dominated rather than enthalpically driven since $|\Delta H^\theta| < |-T\Delta S^\theta|$. The negative values of ΔG^θ and the positive values of ΔH^θ suggested that the adsorption process is spontaneous and endothermic. The value of ΔH^θ (37.262 kJ/mol) suggested that the electrostatic interaction is the dominant mechanism for the adsorption of cationic starch on kaolin. The fractional coverage decreased with increasing temperature, consistent with a reduced hydrodynamic diameter and a more contracted polymer conformation.

Keywords: Cationic starch; Kaolin; Flocculation; Adsorption; Kinetics; Thermodynamics

1. Introduction

Cationic starch derivatives are important commercial products that find wide applications in fields such as papermaking, spinning and weaving, petroleum well drilling, water treatment, medicine, daily chemicals and floatation. Cationic starch, especially those with high degree of substitute, are the most common type of nature polysaccharides derivative flocculants investigated due to the efficient flocculation for suspensions of inorganic or organic matter having a negative charge 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 [1–10]. 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.

The flocculation of fine particle suspensions are critically dependent on many physicochemical factors including particle size and distribution, solid concentration, pH and ionic strength of the suspending medium, molecular weight and charge density of the flocculants, adsorption density and conformation of the adsorbed flocculants. But the most important influence affecting the extent and mechanism of flocculation is dependent primarily on the nature of adsorption of the polymer on the particle surface and also the conformation of the adsorbed polymer. Sableviciene et al. [1], Bratskaya et al. [2], Jäinström et al. [4], and Björklund and Wågberg [7], 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. Flocculation does not require high or complete coverage of the particle surface by the adsorbed polymer. Besra et al. [11] proposed that for flocculation of kaolin suspension the optimum flocculant concentration for obtaining the highest settling rate corresponds to about 50% coverage of the particle surface by the adsorbed flocculant. Nyström et al. [10] 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

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enhanced with increased adsorption. Jäinström et al. [4] 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 Ritchie [12] 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.

Although the past works indicated cationic starch could be effective flocculants for wastewater treatment, there has been very little work undertaken examining the flocculation and adsorption kinetics of cationic starch for 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-flocculation kinetics are not always so simple. The underlying aim of this current work is to emphasize the kinetics of cationic starch adsorption and flocculation in flocculated kaolin systems and to show the importance of investigating the kinetics of adsorption and flocculation to fully understand the flocculation phenomena. Adsorption isotherms and thermodynamic parameters of the adsorption were also investigated.

2. Experimental

2.1. Materials

Cationic starch derivatives (2-hydroxy-3-trimethylammonium-propyl starch chloride) with degree of substitution (DS 0.47), corresponding to 47 quaternary ammonium groups per 100 glucose units, were synthesized according to the route described elsewhere [13]. Common corn starch (industrial grade) purchased from Dacheng Corn starch Co., Ltd. (Jilin, china) was used as a raw material. Substitution degree of derivatives was determined by semimicro *Kjeldahl* method as described in [14]. Cationic starch solution with concentration 1 and 5 g/L were prepared by dissolving an appropriate amount of starch with stirring for 1 h at 60 °C and then for 24 h at room temperature.

A kaolin sample was procured from Xinong Chemical Company Limited. 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); particles larger than 325 mesh: 0.01% maximum; the specific surface area measured by BET method was 10.62 $\mathrm{m^2\,g^{-1}}$; density of kaolin: 2.25 $\mathrm{g\,cm^{-3}}$; moisture 0.3% maximum; silica: 53 ± 0.5 %; alumina: 44 ± 0.5 %; ferric oxide: 0.5%, titania: 0.2%; loss on ignition 0.5%.

Sodium chloride was used as a supporting electrolyte at a concentration of 0.01 mol/L to maintain constant ionic strength. Dilute solutions of NaOH and HCl were used for pH adjustments.

2.2. Adsorption experiments

The adsorption capacities of water-soluble cationic starches onto kaolin particles were determined by the depletion method. One gram of kaolin was suspended in 100 mL of 0.01 mol/L NaCl solution at predetermined temperature and stirred for 10 min with a magnetic stirrer. Cationic starch solution (of required concentration) was added to the kaolin dispersion and the stirring was extended for predetermined time. Although adsorption is a fast process, we found that complete adsorption and saturation were attained after 1-day. During required time for 1–30 min 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 spectrophotometer (Spectrophotometer-722, Shanghai Qinghua Analytical Instruments Factory, China) and colloid titration procedure [1]. The amount of adsorbed starch (Q) was calculated using the difference between known initial starch concentration and concentration measured in supernatant.

$$Q = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where C_0 and C_t are the initial and residual concentration of cationic starch in the suspension at time t; V the volume of the suspension; m is the mass of the kaolin powder, respectively.

2.3. Flocculation experiments

A 2-g of kaolin was dispersed in a 250-mL beaker with 150 mL water with 0.01 mol/L 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 250-rpm for 1–5 min. The flocs were then allowed to settle down for predetermined time periods. A clarified layer of liquid was formed in the upper part of the beaker. At the end of the settling period, the suspension was allowed to flocculate for predetermined time periods and then a fixed volume was removed by suction, filtered, dried, and weighed.

3. Results and discussion

3.1. Flocculation kinetics

The kinetics of flocculation depends on the rate of different processes, namely, the rate of the transport of polymer molecules to the suspended particles, the rate of adsorption of macromolecules on the surface and the time scale necessary to reach the equilibrium state of the polymer layer, the rate of aggregation of particles having adsorbed polymers, and frequency of collisions of particles with adsorbed polymer to form flocs.

3.1.1. Effect of contact time on adsorption

Fig. 1 shows the variation of adsorption capacity with time for different initial flocculant concentration at 25 °C. The adsorption rate of cationic starch is found to be very rapid during the initial 1 min and thereafter the adsorption of cationic starch decreases. No significant change in the adsorption of cationic starch is observed after about 10 min. The results show that a rapid

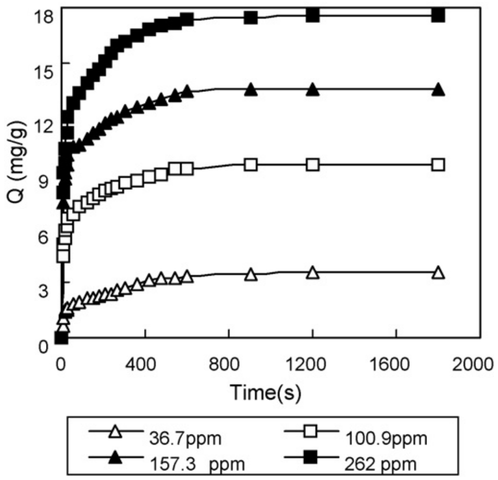

Fig. 1. Adsorption capacities of cationic starch on kaolin as a function of time (pH 5.0; temperature, 25 °C; NaCl concentration, 0.01 mol/L).

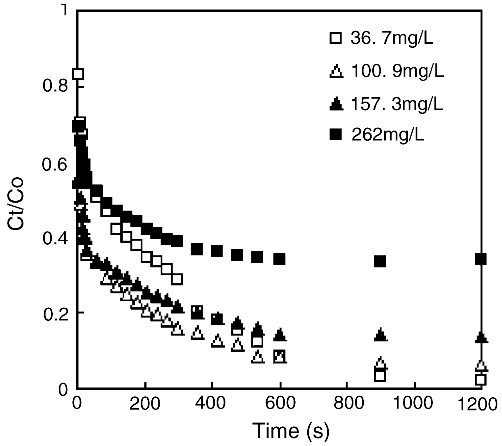

Fig. 2. Dimensionless concentration as a function of time for cationic starch at various initial concentrations (pH 5.0; temperature, 25 °C; NaCl concentration, 0.01 mol/L).

increase in cationic starch adsorption occurred within 1 min with more than 90% of equilibrium adsorption completed in all cases. Fig. 1 shows that the adsorption of cationic starch onto kaolin attains about 99% of their equilibrium adsorption density within 5 min. Therefore, after 5 min contact time, a steady state approximation was assumed and a quasi-equilibrium situation was accepted. Since the time of flocculation in our experiments is 5 min, the adsorption of cationic starch on kaolin can be assumed to be close to the equilibrium adsorption condition. Hence, in each case, 5 min can be considered as the equilibrium time required for maximum adsorption of flocculant.

As shown in Fig. 1, the adsorption capacities increase with increasing initial cationic starch concentration. The amount of cationic starch adsorbed increases from 3.609 to 17.59 mg/g by increasing initial cationic starch concentration from 36.7 to 314.58 ppm, respectively. Adsorption results indicated the adsorption of cationic starch is fast at the initial stages of the treatment time, and thereafter, it becomes slower near the equilibrium. 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 [15]. Then, a slower adsorption would follow as the available adsorption site gradually decreases and repulsive forces increase.

3.1.2. External mass transfer model

A commonly used empirical model [16] was used in this work to calculate the rate of the transport of cationic starch molecules to the kaolin particles, k_f.

$$\frac{\mathrm{d}C_t}{\mathrm{d}t} = -k_f S_S (C_t - C_S) \tag{2}$$

where C_t is the cationic starch concentration in fluid phase at t; C_s the related to the fluid phase concentration at the external surface; k_f the external mass transfer coefficient; S_S is the surface area for mass transfer to the particle assuming smooth spherical particles.

At $t = 0$, $C_t = C_0$, Eq. (2) becomes

$$\left[\frac{\mathrm{d}(C_t/C_0)}{\mathrm{d}t}\right]_{t=0} = -k_f S_S \tag{3}$$

The plot of C_t/C_0 versus t was shown in Fig. 2. At $t = 0$, the plot of C_t/C_0 will yield a slope of $-k_f S_S$, from which k_f can be obtained and presented in Table 1. The data indicate that, as expected, the concentration of cationic starch decreased as contact time progressed indicating that flocculant has been transferred from the solution phase to the surface of kaolin particles. The data also suggest that the transport rate is rapid with 50% transport, depending on initial concentration, occurring within

Table 1
Effect of initial concentration of cationic starch (C_0) on external mass transfer rate coefficient (k_f), rate constant of adsorption (k), and initial adsorption rate (h)

C_0 (ppm)	External mass transfer model		Pseudo-second-order model		
	k_f ($\times 10^{-2}$ cm/s)	R^2	k (g mg^{-1} s^{-1})	h (mg g^{-1} s^{-1})	R^2
36.7	8.47	0.9180	1.727×10^{-2}	0.1218	0.9948
100.9	5.70	0.9520	1.048×10^{-2}	0.7581	0.9973
157.3	5.62	0.9927	7.666×10^{-3}	1.2038	0.9953
262	4.65	0.9994	5.023×10^{-3}	1.3153	0.9972

R^2 correlation coefficient.

the first minute of the experiment. After 1 min there is a gradual decrease in the rate of transport as the experiment proceeds. From Table 1, external mass transfer rate (k_f) decreased with the increase in initial flocculant concentration. This is in agreement with adsorption equilibrium theory, as the influence of initial flocculant concentration on external mass transfer is dependent on the slope of the operating lines on equilibrium isotherms, i.e., the lines joining C_0–C_e. The higher the C_0 value the lower the sloped of the operating lines are, and therefore the driving force for mass transfer decreases.

3.1.3. Pseudo-second-order model

In order to analyze the rate of adsorption of cationic starch on kaolin particle surface for the present study, characteristic constants of the adsorption were determined using a pseudo-second-order equation based on pseudoadsorption equilibrium capacity of the solid phase. The term "pseudo" is used to denote the nonequilibrium nature of the isotherm [17]. The pseudo-second-order equation [18] is expressed as:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t \tag{4}$$

where k is the rate constant of the adsorption (g mg^{-1} s^{-1}), Q_e the amount of cationic starch adsorbed at equilibrium (mg g^{-1}) and Q_t is the amount of adsorbed cationic starch on the surface of kaolin at any time t (mg g^{-1}).

The initial adsorption rate, h (mg/g s), as $t \to 0$ can be defined as: $h = kQ_e^2$, then Eq. (3) becomes

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e}t \tag{5}$$

Fig. 3 shows the plot of t/Q_t versus t for the adsorption of cationic starch on kaolin at different initial concentration. Highly significant linear regression curves ($R^2 > 0.98$) supported the adsorption model used, which indicated that the adsorption kinetics followed the pseudo-second-order model. The values of k and Q_e can be obtained from the intercept and the slope of the line, respectively. The results are listed in Table 1 for each initial concentration.

From Table 1, it is evident that h increases with the increase in initial flocculant concentration, which is in good agreement with the uptake results shown in Fig. 3. It is also evident that the value of k decreases as the initial concentration increases. The k value decreased with increasing initial concentration, meaning 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 starches on kaolin surface. It is also evident from Fig. 1 that the adsorption processes for cationic starch is highly dependent on the initial concentration of cationic starch.

3.1.4. The kinetics of aggregation of particles

Cationic starch addition produced a fast flocculation process that decreased the concentration of the kaolin particles to a minimum value, as shown in Fig. 4. With 36.7 ppm of cationic starch, the final concentration of the kaolin particles was lower because of the formation of relatively weak flocs that were broken by hydrodynamic shear forces under the conditions of testing. This is due to the low dosage and the number of the positive charge of the cationic starch that do not favors the flocculation by "bridging" and charge neutralization. The rate of flocculation is slow and the rate of deflocculation is rapid. Fig. 4 shows that the particle aggregation took place during the first 60 s after the cationic starch addition, producing large flocs whose stability could be hard enough to maintain at 250 rpm. As was expected, the concentration of the kaolin particles after flocculation decreased with increasing the flocculant dosage. However, this decrease was not pronounced for higher flocculant dosage (262 ppm) as compared with intermediate flocculant dosages (157.3 ppm). The influence of flocculant dosage can be explained because bigger flocks are formed when flocculant dosage increases. Besra et al. [19] have observed at pH values above 2.2, the kaolin surface becomes net negatively charged. Adding cationic starch 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 kaolin particles still have free active sites

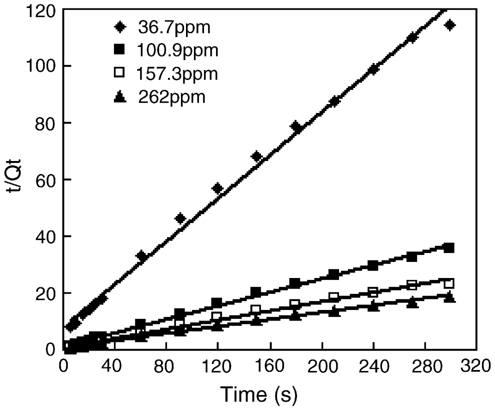

Fig. 3. t/Q_t vs. time plots for cationic starch adsorption on kaolin at various initial concentrations (pH 5.0; temperature, 25 °C; NaCl concentration, 0.01 mol/L).

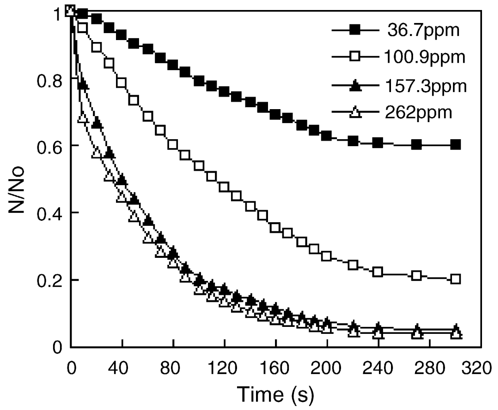

Fig. 4. Kinetic curves of flocculation of kaolin by cationic starch at different initial concentration (pH 5.0; temperature, 25 °C; NaCl concentration, 0.01 mol/L).

that can be adsorbed on the free surface of other particles. This process results in "bridging" between kaolin 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 would result in the optimal rate value for the aggregation of particles. After this situation, higher flocculant dosage may impart a positive electric charge to the suspended particles high enough to cause mutual repulsion. In addition, at higher dosage starches covers most of the available sites on each particle and bridging becomes negligible. The overall result is redispersal of the flocs because of electrostatic repulsion. Therefore, the rate for the aggregation of particles decreased.

The kinetics of the aggregation of particles, deflocculation and reflocculation processes was studied by following Smoluchowski classical model [20,21], based on the existence of two simultaneous processes: the aggregation of particles, with second-order kinetics, and the aggregate breakage, with first-order kinetics.

$$\frac{\mathrm{d}(N/N_0)}{\mathrm{d}t} = -N_0 k_1 \left(\frac{N}{N_0}\right)^2 + k_2 \frac{N}{N_0} \tag{6}$$

where N is the number concentration of the kaolin particles at t; N_0 the number concentration of kaolin particles at $t=0$; k_1 and k_2 are the kinetic constants for the aggregation of particles and kinetic constants for the aggregate breakage, respectively. This relationship allows us to compare the kinetics of aggregation of particles and the aggregate breakage at different initial concentration. The relationship between both types of kinetics allows us to obtain the equilibrium situation towards which the system tends in each case.

The rate constants obtained from the plot of N/N_0 versus t curve are given in Table 2. The rate constants for the aggregation of particles (k_1) increased and the rate constants (k_2) for the aggregate breakage decreased with increasing in flocculant dosage (Table 2). This shows that the flocks formed with high dosage of cationic starch were harder than the flocs formed with low dosage of cationic starches. This could indicate that there are more junction points among particles and that those junctions are stronger. k_1 obtained with 262 ppm of cationic starch was similar to the one obtained with 157.3 ppm. The steric repulsive forces explain the lower rate constants for the aggregation of particles with 262 ppm of cationic starch. When the cationic starch dosage is larger than 157.3 ppm, there are steric and electrostatic repulsion forces among particles, because the amount of the cationic starch adsorbed on particle surfaces is higher than 90% of the maximum adsorption and because the particles are positively charged. This causes the flocculation rate to decrease, as shown by the k_1 values presented in Table 2. These results demonstrate that cationic starch overdose affects the flocculation kinetics and show the competition between cationic starch adsorption and bridge formation, which affects floc properties. However, k_2 obtained with 262 ppm of cationic starches was smaller than the one obtained with 157.3 ppm. This indicates a moderate excess of cationic starch could improve the floc stability and increase the floc strength. But a large excess of cationic starch affects the flocculation kinetics and the floc properties.

3.1.5. *Frequency of collisions of particles*

Investigations of flocculation kinetics of suspensions are important for understanding the flocculation mechanism and for process control of solid–liquid system separations. From the literature [15,22,23], it is known that the order of flocculation process is mostly bimolecular.

$$\left(\frac{N_0}{N_t}\right)^{1/2} = 1 + \frac{1}{2} k N_0 t \tag{7}$$

where N_t is the number concentration of the kaolin particles at time t, and k is the rate constant for collisions between the singlets. N_0 values for a known weight of kaolin were calculated by considering the particle diameter (2 μm) and density of kaolin (2.25 g cm^{-3}). For a 1 g kaolin sample, N_0 was calculated to be 1.062×10^8. Similarly, knowing the weight of particles flocculated in a given time period, one can calculate N_t (here the assumption is that the portion of kaolin which did not flocculate are singles). A plot of $(N_0/N_t)^{1/2}$ against t should give a straight line with an intercept of 1 for a bimolecular process (Fig. 5). The rate constants (k) were obtained from the slope of $(N_0/N_t)^{1/2}$ versus t curve and are given in Table 2.

From Table 2, it is clear that the rate constant (k) increases as the cationic starch concentration increases. At a low dosage of 36.7 ppm, the rate constant is very small but shows a 10-fold increase at the higher cationic starch concentration. In the case of low dosage, the number of cationic starch molecules is too low for both charge neutralization and bridging effects. Therefore, k is low. The enhancement in the rate constant (k) with the increase of flocculant concentration could be ascribed to the greater availability of flocculant in the vicinity of kaolin particles. As a result, the chances for molecular collisions between cationic starch and kaolin will be greater. Once this is the case, the adsorption of cationic starch onto kaolin surface would be

Table 2
The rate constant for flocculation of kaolin at different initial concentration

C_0 (ppm)	Kinetics of aggregation of particles		Frequency of collisions of particles	
	k_1 ($\times 10^{-11}$ count^{-1} s^{-1})	k_2 ($\times 10^{-9}$ s^{-1})	k ($\times 10^{-11}$ s^{-1})	R^2
36.7	2.80	10.23	2.07	0.9677
100.9	5.50	9.973	7.72	0.9882
157.3	7.40	8.187	24.40	0.9776
262.0	7.00	7.525	26.93	0.9783

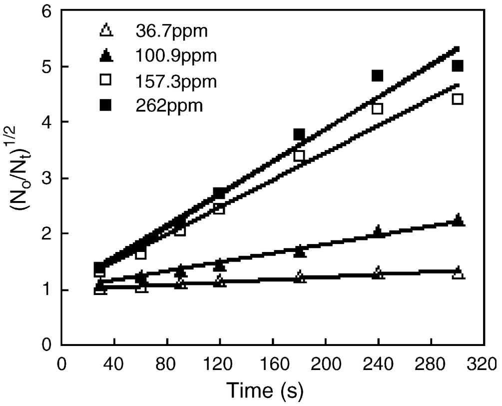

Fig. 5. $(N_0/N_t)^{1/2}$ as a function of setting time at different initial concentration (pH 5.0; temperature, 25 °C; NaCl concentration, 0.01 mol/L).

favored. It was further demonstrated that the dosage of the starch might be adjusted to control the flocculation behavior.

The rate constant for all initial concentrations (Table 2) with extremely low values ($<10^{-10}$) for the kinetic model of aggregation of particles and frequency of collisions of particles compared with those for external mass transfer model and pseudo-second-order kinetic models for the adsorption of cationic starch onto kaolin strongly suggest that the rate-limiting step may be the process of aggregation of particles and frequency of collisions of particles.

3.2. Adsorption isotherms

The distribution of cationic starches between the solid adsorbent phase and the liquid phase at equilibrium, which are the basic requirements for the design of adsorption systems, can be best expressed by adsorption isotherms. All adsorption isotherms for cationic starches onto kaolin particles at different temperature were fitted to the following Langmuir adsorption isotherm model.

$$\frac{C_e}{Q} = \frac{1}{Q_m K_n} + \frac{C_e}{Q_m} \tag{8}$$

where C_e presents the equilibrium concentration of cationic starche (ppm) in the solution; Q is adsorbed amount of cationic starche (mg/g); Q_m represents the maximum monolayer adsorption capacity (mg/g) and K_n is a constant related to the energy of adsorption (L/mg).

Fig. 6 shows that the adsorption capacities increase with increasing in temperature, suggesting that the adsorption is endothermic in nature. Similar endothermic results have also been reported for several related cationic starch adsorption studies [1–4].

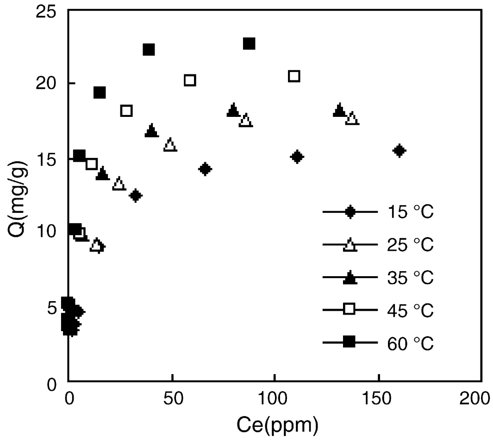

Fig. 6. Pseudoadsorption isotherm at different temperature (pH 5.0; NaCl concentration, 0.01 mol/L).

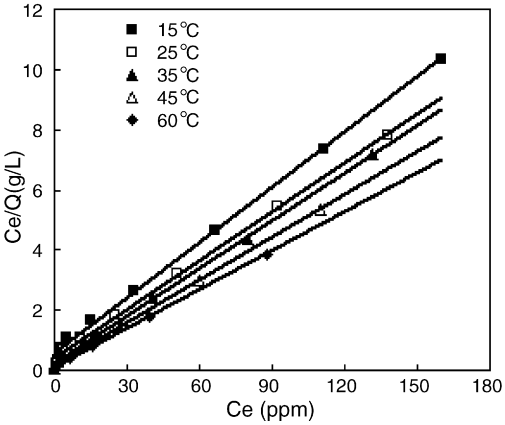

Fig. 7. Langmuir plot of adsorption (pH 5.0; NaCl concentration, 0.01 mol/L).

The maximum monolayer adsorption capacity (Q_m) and the equilibrium constants (K_n) calculated from the slope and the intercept of linear plot of C_e/Q versus C_e (Fig. 7) together with the correlation coefficients are summarized in Table 3. It may be stated that the experimental data were well correlated ($R^2 > 0.99$) by the Langmuir adsorption isotherm, which suggests that the cationic starch form monolayer coverage on the kaolin surface.

In order to gain an insight into the adsorption mechanism involved in the adsorption process, thermodynamic parameters for the present system were calculated. The variation in the free energy (ΔG^θ), apparent enthalpy change (ΔH^θ) and entropy

Table 3
Thermodynamics parameters for flocculant adsorption onto kaolin at different temperature

Temperature (°C)	Q_m (mg/g)	K_n (L/mg)	R^2	ΔH^θ (kJ/mol)	$T\Delta S^\theta$ (kJ/mol)	ΔG^θ (kJ/mol)	Fractional coverage ($\times 10^{-2}$)
15	16.3132	28.7053	0.9975	37.262	45.304	−8.042	9.247
25	18.4502	46.5326	0.9974	37.262	46.781	−9.519	8.176
35	18.9036	86.2784	0.9991	37.262	48.682	−11.420	7.980
45	21.2314	111.981	0.9978	37.262	49.974	−12.480	7.105
60	23.2558	240.246	0.9979	37.262	52.445	−15.183	6.487

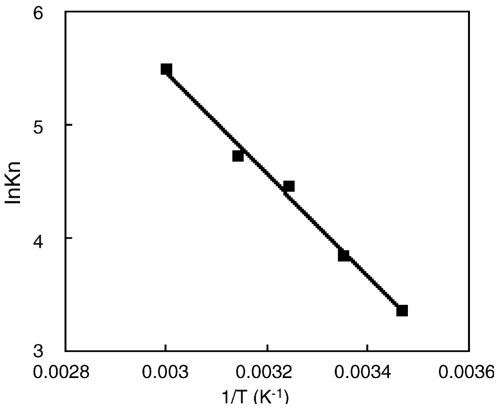

Fig. 8. van't Hoff plot of adsorption equilibrium constant, K_n using Langmuir constant.

change (ΔS^θ) were calculated using the following thermodynamic functions:

$$\Delta G^\theta = -RT \ln K_n \tag{9}$$

$$\Delta H^\theta = -\left[R\frac{\mathrm{d}\ln K_n}{\mathrm{d}(1/T)}\right] \tag{10}$$

where R is the universal gas constant; T the absolute temperature (K); K_n is the Langmuir constant.

Fig. 8 shows the van't Hoff plots of $\ln K_n$ versus $1/T$. The value of ΔH^θ was determined from the slopes. Table 3 listed the calculated thermodynamic parameters. It is noted that all ΔG^θ values listed in Table 3 are negative. This suggests that the adsorption process is spontaneous with high preference of cationic starch for kaolin. ΔG^θ was more negative with increasing temperature, which suggested that higher temperature facilitates the flocculation. As it is reflected from the positive value of ΔH^θ, the adsorption process was endothermic which is responsible for increase in adsorption as the temperature increased. The data not only indicate that the adsorption of cationic starches onto kaolin is more favorable at increasing temperatures, but also suggest that the adsorption process is dominated by entropic rather than enthalpic effects since $|\Delta H^\theta| < |-T\Delta S^\theta|$.

The variation of energy for physical adsorption is generally small than that of chemisorption. Typically, ΔH^θ for physical adsorption ranges from 0 to 40 kJ/mol, compared to that of chemical adsorption ranging from 40 to 800 kJ/mol [25]. As shown in Table 3, the value of ΔH^θ (37.262 kJ/mol) was higher than those corresponding to physical adsorption but near the lower limit of corresponding chemical adsorption. This would suggest that the adsorption process might be considered as physical adsorption in nature. Moreover, the chemical sorption may be involved in cationic starch adsorption on kaolin particles.

3.3. Reversibility and conformation of the adsorbed cationic starch

To establish the nature of adsorption, desorption experiments were carried out by washing the cationic starch treated suspension with distilled water. The kaolin was treated with cationic starch in a manner similar to that for adsorption studies except that at the end of the equilibration time, the contents were filtered and washed with measured amount of distilled water till the filtrate did not show any trace of measurable quantity of cationic starch. The concentration of cationic starch in the filtrate liquid is reported as the amount desorbed on washing, and is presented in Table 4. With the decrease of flocculant dosage, the formed flocs were slowly destroyed, as shown by the slow increase in the values of percentage of flocculant desorbed by washing. It is generally believed that polyelectrolyte induces the formation of irreversible flocs [20]. Partial kaolin reflocculation is possible with low doses of cationic starches, while an overdose of cationic starches induces the formation of irreversible flocs. Therefore, although the covering grade was high and the charge of the particle surface was reverse, high doses produce stable flocs. As shown in Table 4, with 36.7 and 100.9 ppm of cationic starches, it clearly shows that by washing about 70% and 65% of the adsorbed cationic starch was desorbed, respectively. The fact that they are removable by simple washing suggests that they could have been adsorbed on kaolin surface by physical adsorption. Such physical adsorption could be a result of electrostatic interaction between negatively charged kaolin surfaces and positively charged cationic starch. Moreover, the magnitude of ΔH^θ obtained from thermodynamic study also supports that the adsorption process was a typical physical process. The balance of above 40% cationic starch at higher dosage, which could not be desorbed by simple washing, could have adsorbed on kaolin surface through chemisorption. The interaction between cationic starch and kaolin surface may be considered to occur via hydrogen bonds. The mechanism of adsorption involving hydrogen bonding of hydroxyethyl groups to silanol or aluminol groups on the kaolin surface is proposed in this case. Moreover, the magnitude of ΔH^θ (37.262 kJ/mol) obtained from thermodynamic study also supports that the chemical sorption may be involved in the cationic starch adsorption on kaolin.

Since the best flocculation was obtained at pH 5.0 (where the cationic starch molecules are believed to be in the coiled form [19]), as a rough approximation the cationic starch molecules

Table 4
The result of desorbed studies and the surface coverage

C_0 (ppm)	Total amount of flocculant adsorbed (mg/g)	Amount of flocculant desorbed (mg/g)	Percentage of flocculant desorbed by washing (%)	Fractional coverage ($\times 10^{-2}$)
36.7	3.3536	2.3708	70.69	4.795
100.9	9.2361	6.0873	65.91	5.690
157.3	13.4275	7.9746	59.39	6.021
262	17.3257	9.1613	52.88	7.763

were considered to be spherical too. The surface coverage was calculated by considering kaolin particles to be spherical. The size of a polymer patch was calculated by using the formula, size = πR_{H}^2, where R_{H} is the hydrodynamic radius (R_{H}) of adsorbed cationic starch. Besra et al. [11] measured the hydrodynamic radius (R_{H}) of adsorbed polymer and found it to be close to the gyration size ($\langle S^2\rangle^{1/2}$), which is related to the specific surface area (S_{A}) and specific monolayer adsorption (Q_{m}) by the following expression:

$$Q_{\mathrm{m}} = \frac{S_{\mathrm{A}}M}{\pi\left(\langle S^2\rangle^{1/2}\right)^2 N} \tag{11}$$

where M is the number-average molecular weight of adsorbed polymer; N is the Avogadro's number (6.023×10^{23}). Since S_{A}, M and N are constants, the value of gyration size ($\langle S^2\rangle^{1/2}$) can be estimated directly from the above equation.

We have used the adsorption data presented in Table 3 to calculate the surface coverage. From the cationic starch concentration one can calculate the number of molecules per kaolin particle (total weight of kaolin taken for each flocculation experiment was 1 g). By multiplying the number of molecules/particle with the polymer patch size, one gets the total patch area on the particle surface. Since the particle surface area is known (the diameter being known), one can calculate the fractional surface coverage as total patch area/particle area ($4\pi r^2$). Some typical values are given in Tables 3 and 4.

As shown in Table 3, the surface coverage decreased as the temperature increased. This attributed to the decrease of the hydrodynamic radius (R_{H}) of adsorbed polymer with increasing in temperature. Hydrodynamic diameter of cationic starch decreased with increasing temperature, consistent with a reduced cationic starch–solvent interactions and a more contracted polymer conformation. The decrease of the hydrodynamic radius of nonionic polyethylene oxide and anionic polyacrylamide adsorption on kaolin by increasing temperature has been observed by Mpofu et al. [24]. Moreover, as the temperature was increased, the floc structures became more open with larger voids, which, under shear, were easily destroyed. So the surface coverage decreases with increasing temperature.

From Table 4, the surface coverage increases with the increase of initial flocculant concentration. When the dosage of flocculant was 36.7 ppm, the coverage grade of the particles was low because the adsorbed amount of cationic starches was six times lower than the maximum one. Under these conditions, the configuration of the adsorbed chains may evolve toward a flat conformation and the flocculation grade may decrease. This potential flattening would be slower than the aggregation process. With this low dosage, the charge density is low, and the steric repulsion is negligible because of the low coverage grade. Therefore, for low doses of cationic starches induced aggregation despite the low coverage grade, the mechanism induced by cationic starches may be the fast formation of bridges. When the first chains adsorb onto a particle, they can form bridges with other particles and part of the cationic starch could be adsorbed on these aggregated particles before the coverage grade reaches such a value that steric repulsion takes place. In that case, flocs are stable, which is consistent with the hypothesis of flattening because the high coverage grade avoids the flattening of the cationic starch. When the dosage is 157.3 or 262 ppm, the coverage of the surface of the particles would be high enough to limit the polymer flattening. The higher coverage grade limits the polymer flattening, and the minimization of electrostatic repulsive forces among particles. And the higher coverage grade there were the higher number of junction points, the flocs were more stable than the ones induced by the low dose because polymer flattening is limited at a high coverage grade.

4. Conclusions

Adsorption results indicate the adsorption of cationic starch is fast at the initial stages of the treatment time, and thereafter, it becomes slower near the equilibrium. The rate of the transport of cationic starch molecules to the kaolin particles is very rapid. The driving force for mass transfer decreases with the increase of initial flocculant concentration. Adsorption kinetics of cationic starch follows pseudo-second-order model ($R^2 > 0.98$). The adsorption rate constant was found to increase with the increase in cationic starch concentration. The rate constants for the aggregation of particles increase as initial flocculant concentration progresses, but after 157.3 ppm it decreases. The rate constants for the aggregate breakage decrease with increasing initial flocculant concentration. The increase of the collision efficiency shows that increase in flocculant dosage results in higher rate constants for the flocculation process. The rate of aggregation of particles and frequency of collisions of particles are very slow and the two steps determine the rate of flocculation process.

Thermodynamic parameters indicate that the adsorption process is a spontaneous process. The adsorption data show that the free energy of cationic starch adsorption is strongly temperature-dependent and that cationic starch adsorption onto kaolin particles entropically dominates rather than enthalpically driven. The value of ΔH^{θ} (37.262 kJ/mol) suggest that the electrostatic interaction is the dominant mechanism for the adsorption of cationic starch on kaolin.

The surface coverage decreases with increasing temperature, consistent with a reduced hydrodynamic diameter and a more contracted polymer conformation. The fractional coverage increases with the increase of initial flocculant concentration. The flocs are more stable than the ones induced by the low dose because cationic starch flattening is limited at a high coverage grade.

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