

Flocculation Characteristics of Kaoline Suspensions in Water by Cationic Polyelectrolytes

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Using a simple continuous optical technique, coupled with measurements of zeta potential, the flocculation characteristics of kaoline suspensions of different content(15, 35 and 55 NTU) by several cationic polyelectrolytes, has been examined. The optimum mixing is obtained under a constant stirring of 200 rpm, differently from a general flocculation test. The charge density of a polyelectrolyte is important in determining the optimum dosage and in the removal of kaoline particles. The optimum dosage is less for the polyelectrolyte of higher charge density and is the same regardless of kaoline content. At the dosage, the removal of kaoline particles is higher for the polyelectrolyte of higher charge density and zeta potential of kaoline particles reaches to near zero. The rate of adsorption and flocculation rate have been found to be affected by charge density and molecular weight of a polyelectrolyte and the content of kaoline particles.

Key words : flocculation, kaoline, cationic polyelectrolyte, zeta potential

1. Introduction

Flocculation is an essential process in the solid-liquid separation scheme in water treatment plant. The particles in the range of colloidal size range are not separated by processes, such as sedimentation, filtration or flotation. Flocculation of such particles prior to using these processes is necessary to improve the separation process. It plays an important role in many separations including the removal of particles in the treatment of portable water and the recovery of mineral processing. Since the particles in aqueous system are nearly anionic, they interact strongly with cationic additives, such as inorganic metal coagulants and cationic polyelectrolytes.

Removal of kaoline turbidity from the effluents before discharging into the environment is a problem forced by the clay processing industry. Faust and Aly¹⁾ quote extensive application of kaoline suspensions as a model for natural turbidity of raw surface water or jar-test studies of coagulation and flocculation in the laboratory. Inorganic coagulants, such as alum in combination with lime have been conventionally used for the removal of clay particles in the effluents from clay processing industry as well as from raw water. The sludge formed from such treatment poses disposal problems because of its aluminium content. It has been reported that although not conclusively proved, increasing concern about the residual aluminium, which may be present in water as result of alum treatment, is being expressed by the public in connection with Alzheimer's disease²⁾. Studies on the use of chitosan, which is a polymer of D-glucosamine with an NH₂ group in place of the OH group on carbon-2 of D-glucose and is de-

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scribed as a cationic polyelectrolyte, either alone or in conjunction with inorganic coagulants such as alum and ferric chloride have been reported by Bough³⁾, Bough et al.⁴⁾ and Kawamura.⁵⁾ Application of chitosan in the flocculation of montmorillonite, bentonite and kaoline suspensions have been reported by Peniston and Johnson⁶⁾, Huang and Chen⁷⁾, Pan et al.⁸⁾ and several others. Huang and Chen⁷⁾ and Pan et al.⁸⁾, failed to notice any appreciable flocculation of kaoline suspensions in water by chitosan and reported that the properties of suspended particles have a significant effect on flocculation by chitosan.

The synthetic cationic polyelectrolytes as flocculants, such as copolymers of acrylamide and dimethylaminoethyl acrylate and polydiallyldimethylammonium chloride in the water treatment field have been extensively used^{1,9~11)}. It is known that the behavior of polyelectrolyte flocculant in the treatment of suspended particles can be very greatly affected by its dosage^{9,10,12)} and mixing intensity^{13~17)}, and the destabilization of the particles by a polyelectrolyte flocculant is ascribed to bridging and neutralization of the surface charge and particle potential. Polyelectrolyte flocculation can be considered to comprise the following processes:¹⁸⁾ 1) Transport of polyelectrolyte to the suspended particles. 2) Adsorption of polyelectrolyte adsorption on the particles. 3) Rearrangement of the adsorbed polyelectrolyte chains to give an equilibrium configuration. 4) Collisions of particles with adsorbed polyelectrolyte, forming flocs. 5) Break-up of flocs. These processes may occur simultaneously and they were not well understood by the early 1980's. Thus Gregory and Nelson¹⁹⁾ introduced an on-line technique to be able to obtain immediate information on the state of aggregation of particles in sheared suspensions, from the moment of polyelectrolyte dosing, and a much more complete picture of the flocculation process. This technique of measuring turbidity fluctuations in flowing suspensions²⁰⁾ has been shown that to give good correlation with settling rate of flocs at different mixing times²¹⁾. In addition, Kan and Huang²²⁾ reported that this technique-controlled dosage was significantly lower than the daily dosage for the operators' experience or a periodic jar-test at various raw water conditions ranging from 3.1 NTU to 125 NTU and feeding

flocculant with the former produced higher water quality as well as lower sludge volume than that with the latter.

In the following sections we describe some experiments on the flocculation of kaoline suspensions of different content by several synthetic cationic polyelectrolytes. Particular attention has been paid to the effects of the dosage and mixing intensity on the flocculation of kaoline particles.

2. Experimental

2.1. Materials and Equipment

Analar grade reagents were used and the solutions were prepared with deionized water from a Branstead ultrapure water system.

The kaoline particles were obtained from Aldrich Chem. Co., USA. A stock kaoline suspensions were prepared as follows: 50 g of dry kaoline were added to a 500 mL beaker containing about 400 mL water and a stirrer bar, which was placed on a magnetic stirrer unit. After high speed mixing, the kaoline suspension was adjusted to pH 7.5 with 0.1 N sodium hydroxide in order to disperse the suspension completely. The resulting suspension was made up to 1 L with water and allowed to stand overnight in 1 L measuring cylinder. The top 600 mL from the cylinder was carefully decanted and the lower part was rejected. The suspension was found to contain 2.872 % (W/V), which was determined by taking fixed volume of the suspension and being dry to a constant weight. The particle sizes measured by a Particle Size Analyzer (Malvern 2600, UK) were mainly in the range of 5.33 ~ 6.18 μm (mean 5.74 μm). Working standard solutions (15, 35 and 55 NTU) were prepared by taking 1.24 mL, 2.86 mL and 4.50 mL of the stock solution and diluting to 4 L with water, respectively. The solutions were adjusted to pH 7 with 40 mL of 0.1 N sodium carbonate and 1 N or 0.1 N nitric acid during their preparations. The sodium carbonate was used to fix the initial pH of the solutions.

Cationic polyelectrolytes used were commercial products, kindly supplied by Allied Colloids Ltd. (Now Ciba Speciality Chemicals), UK. These were copolymers of acrylamide and dimethylaminoethyl acrylate (the latter being quaternized

with methyl chloride)(P-A and P-B), poly(2-hydroxypropyl-N,N-dimethylammonium chloride) (an epichlorohydrin-dimethylamine polymer, P-C) and poly(diallyldimethylammonium chloride)(P-D). P-A and P-B were supplied as solids and prepared as 0.01 % aqueous solutions by wetting 0.01 g of the solid with 2 mL of methanol, adding 98 mL of water and agitating for about 12 hrs. P-C (a 50 % active solution) and P-D (a 40 % active solution) were also prepared as 0.01 % aqueous solutions by diluting the products supplied with water. All of the 0.01 % solutions were used within one week of preparation. The properties of the polymers used are given in Table 1.

Table 1. Properties of cationic polyelectrolytes used

Polyelectrolyte	% Cationic	Molecular Weight ^a
P-A	20	$2 \sim 3 \times 10^6$
P-B	40	$2 \sim 3 \times 10^6$
P-C	100	$3 \sim 4 \times 10^4$
P-D	100	$3 \sim 4 \times 10^4$

^acalculated from intrinsic viscosity values given by the manufacturer, using the Mark-Houwink equation ($\eta_{sp} = KM^a$), with estimates of the constants K and a taken from Griebel and Kulicke²³.

Flocculation monitor was a Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK), the principles of which have been given by Gregory and Nelson²⁵. Basically, the intensity of narrow beam of light transmitted through a flowing suspension is monitored by a photo-detector, the output of which consists of a steady (dc) component and a much smaller fluctuating (ac) component.

The flocculating suspension was conveyed through PVC tubing of 2.65 mm internal diameter, by means of a microtube pump (Eyla MP-3N) at a rate of 15 mL/min. The sample continuously passed through the detector of PDA and the monitoring was carried out directly through the transparent tubing. The results were recorded in terms of ratio values. The output of PDA 2000 was conveyed to digital form and logged by a chart recorder. The arrangement is systematically shown in Fig. 1.

Zeta potential of kaoline suspension flocculated under different conditions was measured by a Zeta Potential Meter (Sephy Zetaphoremeter III, France).

The turbidity of kaoline suspensions was measured by a Digital Turbidimeter (Orbeco-Hellige 965, USA).

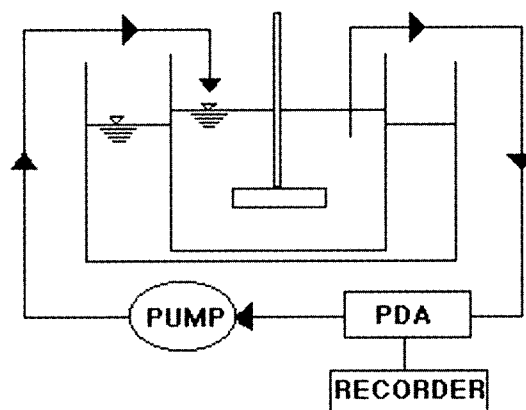


Fig. 1. Flocculation test arrangement.

2.2. Procedure

Flocculation tests were carried out in a 300 mL Pyrex beaker with 200 mL of kaoline suspension containing different turbidity (15, 35 and 55 NTU), which was placed into a water bath to maintain a constant temperature (20 °C). The suspension was stirred by a single flat blade (67 mm × 8 mm × 1 mm thick) with a clearance of 10 mm above the base of the beaker. The blade was centrally located in the beaker and driven by an adjustable speed motor via a thin spindle. A predetermined amount of each cationic polyelectrolyte was added to the suspension with different stirring rate 50 ~ 250 rpm corresponding to average shear rate of about $109 \sim 1214 \text{ s}^{-1}$, calculated from the power input to the unbaffled vessel, for 15 min. The power input was derived from the rotation speed and dimensions of the paddle, using an assumed drag coefficient of 1.8. The average shear rate depends on the power input per unit amount of fluid. During the stirring, ratio values were logged for analysis. Immediately after flocculation test, 25 mL of the suspension was taken from the beaker for zeta potential measurements. The sample was injected into the cell and the mean zeta potential was computed from 10 readings. Standard deviations were usually around 5 % of the mean, or less. The other

suspension was settled for a fixed time and then the supernatant below 2 cm from the surface was taken by a siphon for the residual turbidity measurements.

3. Results and Discussion

3.1. General form of flocculation

Fig. 2 shows a characteristic curve resulting from a typical flocculation test, which was obtained by adding 0.75 mg/L of P-A to a stirred kaoline suspension (35 NTU) and withdrawing sample through the monitor as shown in Fig. 1. The ratio (rms/dc) value was monitored for 15 min with a stirring rate of 200 rpm after polyelectrolyte addition. Since this value gives a sensitive indication of the state of aggregation of the particles, it is termed Flocculation Index (FI) in the following results.

The curve can be arbitrarily divided into 4 regions. In region A, there is little change in the FI with time, which is a consequence of the relatively slow polyelectrolyte adsorption. In this phase, most particles have not yet acquired sufficient polyelectrolyte to become destabilized and particle collisions do not result in aggregate formation. The extent of region A depends on mixing conditions- the more rapid the stirring, the shorter the lag phase¹⁷⁾. As more polyelectrolyte is adsorbed, the collision efficiency increases and so the FI value shows a distinct rise as flocculation begins (region B). In region C, the flocculation has become constant and FI shows a nearly linear rate of increase. Depending on the amount of polyelectrolyte added, adsorption may continue and

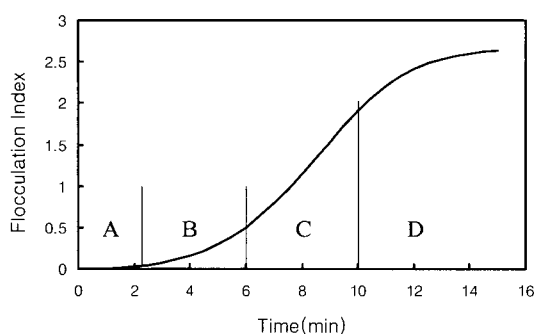


Fig. 2. A typical flocculation curve (P-A : 0.75 mg/L, kaolin suspension: 35 NTU, stirring rate : 200 rpm).

particles could become overdosed, leading to a decrease in collision efficiency and flocculation rate, and hence a levelling-off of the FI (region D). However, even when the amount of polyelectrolyte added is about optimum, the linear rise in FI can not continue indefinitely, because the aggregate (flocs) eventually reach a limiting size, depending on the stirring rate and on the floc strength. This also leads to a maximum in the observed FI value.

3.2. Effect of stirring rate

The thorough mixing of polyelectrolyte throughout a suspension is quite difficult and small droplets of polyelectrolyte solution may persist for some time. This could act as nuclei for floc formation¹⁶⁾. Poor mixing can also lead to local overdosing and restabilization of some particles, which is responsible for the residual haze in some flocculated suspensions¹³⁾. Better mixing could be achieved, in principle, by increasing the applied shear, but there are significant constraints. For instance, it is known that polyelectrolyte molecules can be broken in turbulent flow of moderate intensity and the degradation products may be less effective as flocculants¹⁵⁾. Also, flocs are of limited strength and can be disrupted at high shear rates. Such breakage is often found to be irreversible so that flocs do not re-form from the fragments¹⁴⁾. Both the transport of polyelectrolyte molecules to the particles and particle-particle collisions are rate processes which depend on the applied shear. The acquisition of sufficient polyelectrolyte by a particle to give adequate destabilization may be relatively slow compared to the particle collision rate¹⁷⁾. Also, the reformation of adsorbed polyelectrolyte molecules to a final, equilibrium state may take a long time²⁵⁾ and may also depend on shear rate. It is very likely that polyelectrolyte chains in an extended, non-equilibrium conformation more readily form inter-particle links and hence promote flocculation.

Fig. 3 shows the effect of stirring rate (50 rpm, 75 rpm, 100 rpm, 150 rpm, 200 rpm and 250 rpm corresponding to about shear rate 109 s^{-1} , 199 s^{-1} , 307 s^{-1} , 567 s^{-1} , 869 s^{-1} and 1214 s^{-1} , respectively) on the flocculation of kaoline suspension (55 NTU) during 15 min of stirring at the dosage of P-A 0.75 mg/L, P-B 0.4 mg/L, P-C 0.05 mg/L and

P-D 0.04 mg/L. Generally, the flocculation tests are conducted by rapid stirring(around 200 rpm) for 1~2 min, followed slow stirring(around 50

rpm) for 10~15 min, to allow floc growth. But, under the system used in this study, the flocs are not formed even at the optimum dosage(which is discussed in section 3.3) and so there was little change in FI value during whole stirring time. This result indicates it takes rather a long time to cause the onset of flocculation under above condition. Thus, the flocculation tests were conducted under a constant stirring rate for 15 min.

As shown in Fig. 3, the FI value increases gradually when the stirring rate is increased to 200 rpm(about shear rate 869 s^{-1}). At the rate of 250 rpm(about shear rate 1214 s^{-1}), The FI values are the greatest within nearly 8 min but after that time, they decrease, considered to be due to floc break-up, regardless of the cationic polyelectrolytes used. In the following section, the flocculation tests were conducted at 200 rpm of the optimum stirring rate. Lee and Gregory²⁷⁾ has also used the same stirring rate(200 rpm) in the flocculation of silica suspension by several cationic polyelectrolytes under similar conditions.

Fig. 4 shows the residual turbidity with different settling time(30 min, 1 hr, 2 hr, 4 hr, 6 hr, 12 hr and 24 hr) of the particles, flocculated after the stirring rate of 200 rpm for 15 min. The residual turbidity values are lower for P-A and P-B within 1 hr but are lower for P-C and P-D after 2 hr. This is considered to be by the fact that for P-A and P-B, the flocs formed are larger(shown in FI in Fig. 3) by a strong bridging effect based on higher molecular weight(see Table 1) and so they are settled in a shorter time, but the charged surfaces of kaoline particles are apparently charge-neutralized with less than the corresponding amount of cationic charge because of lower charge density and so they are not completely destabilized. In contrast with P-A and P-B, the flocs formed for P-C and P-D, are smaller because of a much lower molecular weight compared to the former and so they are settled slowly compared to the former, but all the charged surfaces of the particles are completely neutralized by a one-to-one, or a stoichiometric interaction between cationic and anionic sites, because of higher charge density¹¹⁾, and so they are completely destabilized, leading to a lower residual turbidity. This result is similar to Kam and Gregory's report¹¹⁾ that the removal of humic substances at the optimum dosage was higher for

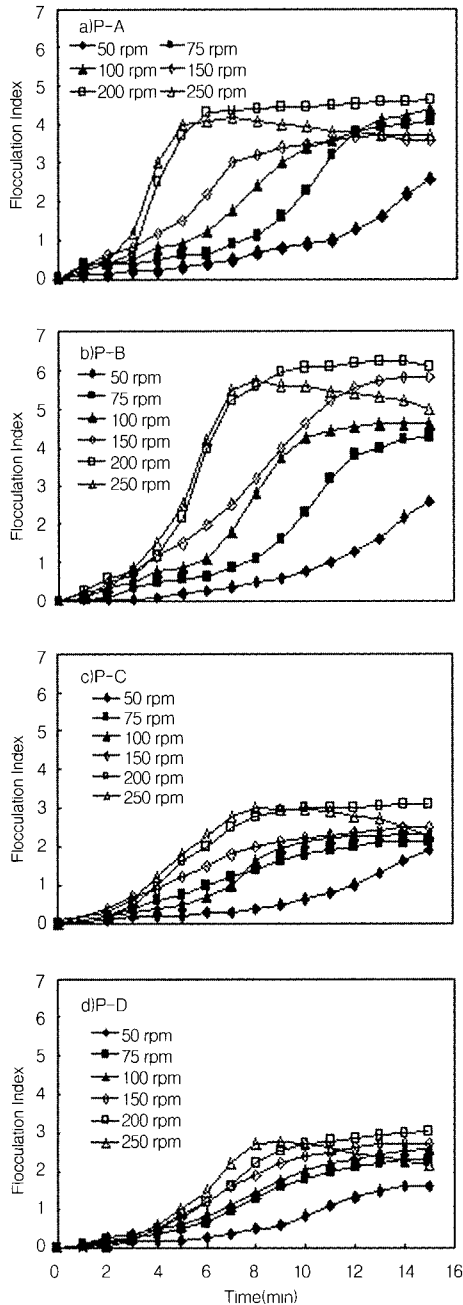


Fig. 3. The effect of stirring rate on the flocculation of kaoline suspension(55 NTU) by cationic polyelectrolytes(P-A : 0.75 mg/L, P-B : 0.40 mg/L, P-C : 0.05mg/L, P-D: 0.04mg/L).

the polyelectrolytes of higher charge density in the flocculation of those by the cationic polyelectrolytes of different charge density and molecular weight. As the residual turbidity seems to be nearly constant after the settling time of 2 hr, the settling time was adjusted to 2 hr in the following section.

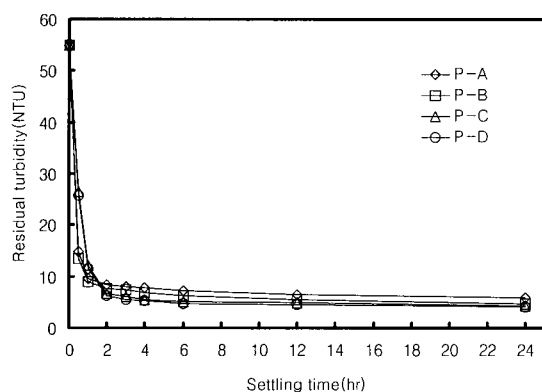


Fig. 4. Dependence of settling time on the residual turbidity of kaolin particles, flocculated under the conditions of stirring rate of 200 rpm in Fig.3.

3.3. Effect of polyelectrolyte dosage

When different amounts of cationic polyelectrolytes were added to the kaoline suspension (35 NTU), the monitor response was shown in Fig. 5. For P-A, the value of FI shows essentially no change at the lowest dosage (0.1 mg/L), indicating little or no flocculation in 15 min. With increasing dosages, there is a reduced lag phase (region A) before flocculation begins and the slope of the curve in region C becomes more steeper, indicating more rapid flocculation. In this case, the optimum dosage appears to be 0.75 mg/L, where the slope is the steepest and the FI value is the greatest (i.e., where the most rapid flocculation occurs and the flocs reach the greatest size). When a higher dosage than the optimum was added, the kaoline particles rapidly acquire excess polyelectrolyte so that the collision efficiency is reduced because of restabilization. At the higher dosage (1.5 mg/L), the FI value also shows little change like as at the lowest dosage (0.1 mg/L). The same phenomena are observed for the other polyelectrolytes.

Comparing the flocculation curves for P-A and

P-B of different charge density (P-A : 20 % charged, P-B : 40 % charged) but the same molecular weight, it can be shown that less amount is required to neutralize particle charge and less time is needed to achieve a certain degree of destabilization for the polyelectrolyte of higher charge density. Also, electrostatic repulsion between polyelectrolyte segments becomes more significant at the higher charge density and this leads to a greater expansion of polyelectrolyte chain. A more expanded chain has a higher collision radius and will adsorb more rapidly, in a stirred suspension.

Comparing the flocculation curves for P-C and P-D with that for P-B, two distinct effects are apparent. The maximum FI value for the former is much lower than that for the latter (i.e., about a half of that for the latter), which is considered to be due to a weak bridging effect based on a lower molecular weight than the latter. The dosage for the optimum flocculation for the former is much less than that for the latter, because of higher charge density of the former (100% charged).

By carrying out the flocculation tests for P-A ~ P-D over a range of concentrations, it is possible to estimate optimum dosages. Operationally, the optimum may be defined as the dosage giving the maximum flocculation and estimates on this base are 0.75 mg/L, 0.4 mg/L, 0.05 mg/L and 0.04 mg/L for P-A, P-B, P-C and P-D, respectively. Although P-C and P-D are both 100 % charged and have the same molecular weight, their optimum dosages are a little different. It is estimated that this finding is ascribed to the difference in molecular structure or to a partial degradation of P-C during the flocculation test.

It is clear that there is a strong inverse correlation between the optimum dosage and the charge density with the most highly charged polyelectrolyte giving the lowest optimum dosage. In fact, the results indicate that, in each case, the optimum dosage corresponds roughly with the same amount of cationic charge, pointing out the importance of charge neutralization. This conclusion is reinforced by the zeta potential data (see Fig. 8). Reversal of the particle charge from negative to positive, occurs at a certain polyelectrolyte dosage, which is close to the optimum flocculation dosage.

3.4. Effect of the kaoline content

The effect of kaoline content (15, 35 and 55 NTU)

on the flocculation of kaoline particles by cationic polyelectrolytes were investigated(Fig. 6). The optimum flocculation is observed at the same dosage of each polyelectrolyte(P-A : 0.75 mg/L, P-B : 0.4 mg/L, P-C : 0.05 mg/L, P-D : 0.04 mg/L) regardless of kaoline content in the range of kaoline

content used in this study. This result is identical Ko's report²⁷⁾ that the optimum dosages of several cationic polyelectrolytes are the same in the flocculation of humic acid in the presence of different kaoline content. However, it can be seen that with

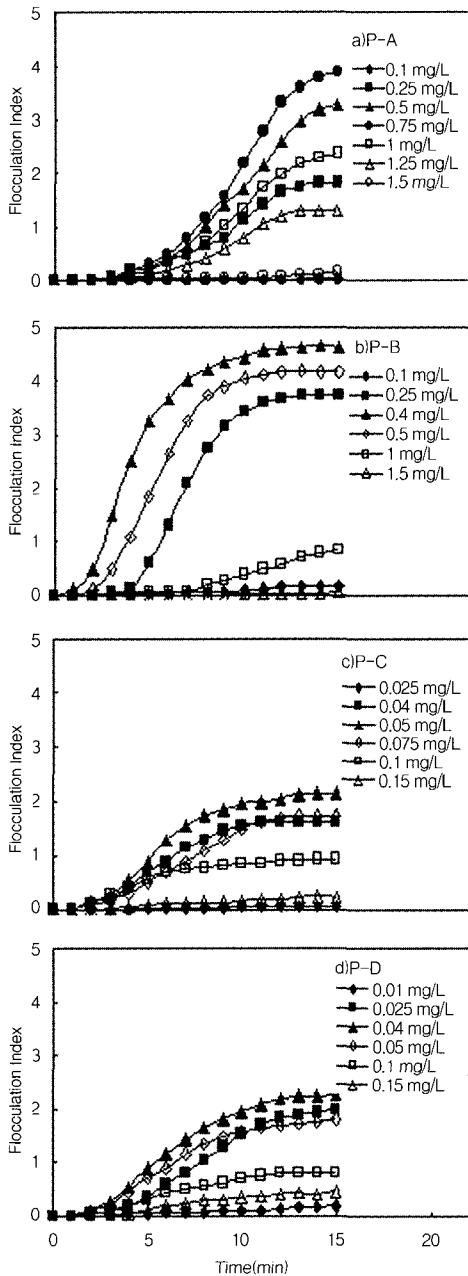


Fig. 5. The effect of polyelectrolyte dosage on the flocculation of kaolin suspension(35 NTU).

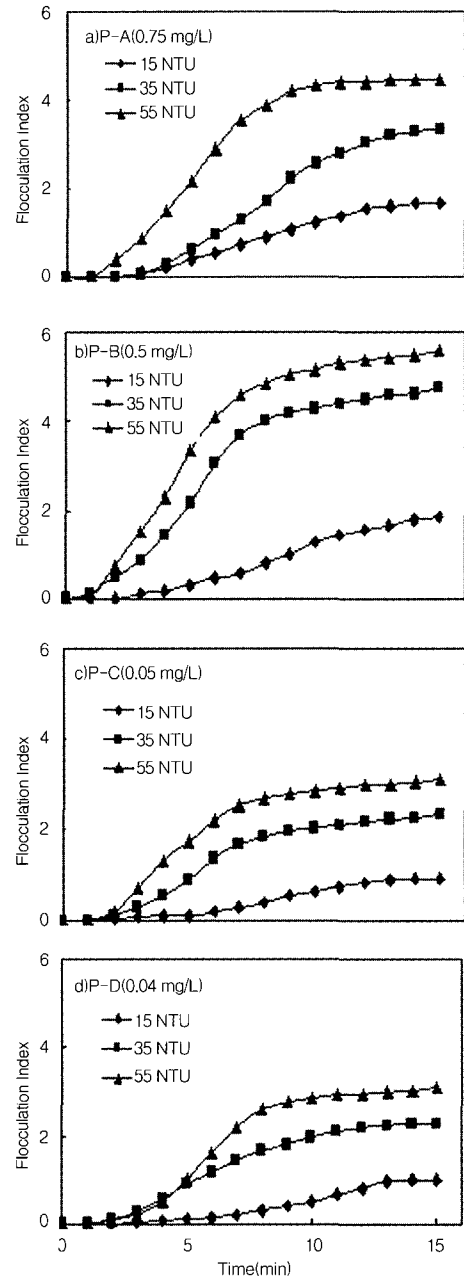


Fig. 6. The effect of kaoline content on the flocculation of kaolin particles at the optimum polyelectrolyte dosage.

increasing kaoline content, the lag phase reduces and the slope in region C becomes more steeper, leading to a higher FI values.

The removal efficiency of kaoline particles with different content at the optimum dosage of each polyelectrolyte is shown in Fig. 7. It can be known that the removal efficiency of kaoline particles is higher with increasing kaoline content and decreased in the order of $P-D \geq P-C > P-B > P-A$ among the polyelectrolytes, indicating the importance of charge density in this system.

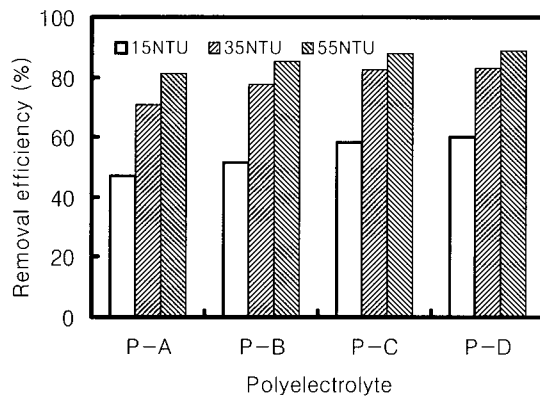


Fig. 7. The removal efficiency of kaoline particles of different content (15 NTU, 35 NTU and 55 NTU) at the optimum polyelectrolyte dosage (P-A : 0.75 mg/L, P-B : 0.4 mg/L, P-C : 0.05 mg/L, P-D : 0.04 mg/L).

Fig. 8 shows the change in zeta potential of kaoline particles with different content after flocculation test for 15 min over a range of polyelectrolyte dosage. As shown in Fig. 8, the optimum dosage of each polyelectrolyte is the same, regardless of kaoline content and at the dosage, the zeta potential of kaoline particles reaches to near zero. From the results obtained in sections 3-3 and 3-4, it can be concluded that the optimum dosage of cationic polyelectrolyte (where the most rapid flocculation occurs and so the maximum FI value is shown) is the dosage to neutralize the charge of the particles.

4. Conclusions

The flocculation characteristics of kaoline suspensions of different content (15, 35 and 55 NTU) by several synthetic cationic polyelectrolytes

has been investigated using a simple monitoring technique. The method gives the useful insight into the behavior of polyelectrolyte flocculants in stirred

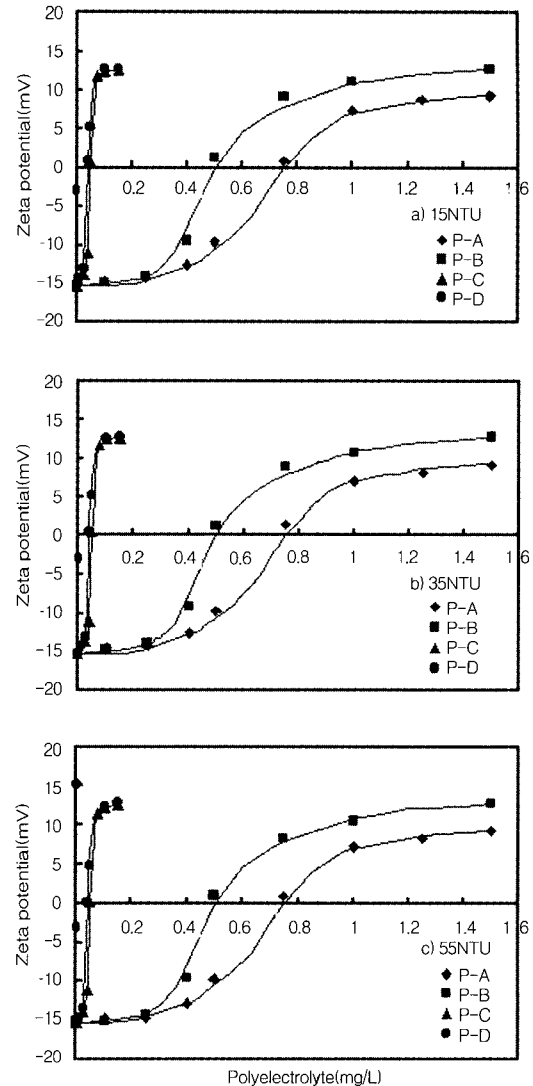


Fig. 8. Zeta potential of kaoline particles of different content (15, 35 and 55 NTU) with the dosage of each cationic polyelectrolyte.

suspensions (i.e., this method gives information on the state of aggregation of particles from the moment of polyelectrolyte addition).

It has been shown that an appreciable lag time has been found between the polyelectrolyte addition and the onset of flocculation. In practice, the adsorption rate may be affected by a number of

factors, such as the stirring rate, the dosage, charge density and molecular weight of the polyelectrolyte.

In this study, the flocs are not formed under a general flocculation test, where it is conducted by rapid stirring for 1-2 min, followed by slow stirring for 10-15 min, indicating that it takes a long time to cause the onset of flocculation. During a constant stirring rate for 15 min, the optimum stirring rate is obtained at 200 rpm (about shear rate 869 s^{-1}).

The optimum dosage where the most rapid flocculation occurs and the flocs reach the greatest size, is lower for the polyelectrolytes of higher charge density, pointing out the importance of charge neutralization. At the dosage, there is a significant reduced lag phase before flocculation begins and the zeta potential of kaoline particles approaches to near zero.

With increasing kaoline content, the lag time reduces, the flocculation occurs more rapidly (i.e., a higher Flocculation Index values are shown), and the removal efficiency of kaoline particles increases. However, the optimum dosage is the same, regardless of kaoline content.

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