

Effects of Polyelectrolyte Dosage, Kaoline Particles and pH on Flocculation of Humic Acid by Cationic Polyelectrolytes

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Using a simple continuous optical technique, coupled with measurements of zeta potential, the effects of polyelectrolyte dosage, kaoline particles and pH on flocculation of humic acid by several cationic polyelectrolytes, have been examined. The charge density of a polyelectrolyte is important in determining the optimum dosage and in the removal of humic acid. The optimum dosage is less for the polyelectrolytes of higher charge density and is the same regardless of the presence of kaoline particles of different turbidity. At the dosage, the removal of humic acid is higher for the polyelectrolytes of higher charge density and the zeta potential of humic acid approaches to near zero. With increasing pH of humic acid, the optimum dosage increases and the flocculation index value obtained at the dosage decreases in the following sequences: pH 7 > pH 5 > pH 9, regardless of polyelectrolytes.

Key words : Flocculation, Humic Acid, Kaoline particles, Cationic polyelectrolyte, Zeta potential, Optimum dosage

1. Introduction

Organic matter in natural waters mainly consists of partially decomposed plant material and most is found as dissolved organic matter (DOM) such as humic substances, hydrophilic acid and simple compounds.¹⁾ Humic substances are complex, heterogeneous, refractory organic compounds with phenolic and alcoholic hydroxyl, carboxyl, keto and quinoid functional groups which may be protonated-deprotonated depending on pH and ranging from several hundred to hundreds of thousands.²⁻⁴⁾ They make up 50-80% of the DOM and their predominant fractions are fulvic and humic acids in natural waters.⁵⁾

The presence of humic substances in water causes a yellow to brown color, may result in the formation of the carcinogenic and mutagenic by-products during chlorination^{6,7)}, can result in

microbial growth in distribution systems, impedes the removal of iron and manganese from the water, and facilitates the transport of contaminants.^{2,8,9)} In addition, they may be adsorbed on the surfaces of many mineral particles as they include both hydrophobic and hydrophilic moieties.¹⁰⁾ A number of processes have been suggested to be involved in mineral humic interactions such as the hydrophobic effect, ligand exchange, electrostatic interactions, van der Waals forces, coadsorption and competition, the dominant process being dependent on the mineral particles under investigation.¹¹⁾ The humic adsorption gives a negative surface charge to the mineral^{12,13)}, influences the colloidal stability and mobility¹⁴⁾, and contributes to the organic carbon, giving a far higher adsorption capacity for other organic compounds and pure clay minerals.¹⁵⁾ For these reasons, it can make them more difficult to remove by conventional water treatment processes.

Several techniques are used to remove organic materials during water treatment and a very common method is flocculation, followed by either filtration, sedimentation or flotation. Since natural organics are nearly anionic over

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the natural waters, they can interact with cationic additives, such as hydrolyzing metal salts and cationic polyelectrolytes. It is frequently found that the optimum dosage of the flocculant is close to that required to neutralize the surface charge carried by the particles, although there are some important exceptions¹⁶⁾, and the charges of the flocculant and the particles are dependent on pH in the solution.^{17,18)}

It is well known that polyelectrolyte flocculation occurs by the mechanisms of bridging and neutralization of the surface charge and particle potential¹⁹⁾, and is composed of 5 processes.²⁰⁾ These processes have not been well understood as they may occur simultaneously. Gregory and Nelson²¹⁾ introduced an on-line monitor 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. It was reported that this monitor-controlled dosage was significantly lower than the daily dosage in the operators' experience or a periodic jar-test at various raw water conditions and feeding flocculant with the former producing a high water quality as well as a lower sludge volume than the latter.²²⁾

In the present paper, the effects of polyelectrolyte dosage, kaoline particles and pH on flocculation of humic acid, have been investigated using several synthetic cationic polyelectrolytes and an on-line monitor enabling an immediate information on the state of aggregation from the moment of polyelectrolyte dosing. The results obtained from this study may provide an useful information on flocculation characteristics between humic acid and cationic polyelectrolytes.

2. Materials and Methods

2.1. Materials and equipment

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

Cationic polyelectrolytes used were commercial products, 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) (P-C) and poly(diallyldimethylammonium chloride) (P-D). P-A and P-B were supplied as solids and prepared as 0.1% aqueous solutions by wetting 0.1 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 0.1% aqueous solutions by diluting the products supplied with water. All of the 0.1% 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	2.3×10^6
P-B	40	2.3×10^6
P-C	100	3.4×10^4
P-D	100	3.4×10^4

^acalculated from intrinsic viscosity values given by the manufacturer, using the Mark-Houwink equation ($\eta = KM^a$), with estimates of the constants K and a taken from Griebel and Kulicke.²³⁾

Humic acid was obtained from Aldrich Chem. Co., USA. The stock solution (5 g/L) was prepared by dissolving 2.5 g of humic acid in 500 mL of 0.1 N NaOH and the solution was filtered through a qualitative (Whatmann) filter paper. A working standard solution (25 mg/L) was prepared by taking 5 mL of this stock solution and 5 mL of 0.1 N Na₂CO₃ and diluting to 1 L to with water. The Na₂CO₃ was used to fix the initial pH of the humic solution. The humic acid solution was then filtered under vacuum through the prewashed 0.45 μ m cellulose nitrate membrane and adjusted to pH 5, 7 and 9 with 0.1 N or 0.01 N HNO₃/NaOH.

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 NaOH 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 were carefully decanted and the lower part was discarded. The suspension was found to contain 2.872% (W/V), which was determined by taking a fixed volume of the suspension and being dried 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 NaOH/HNO₃ during their preparations.

Flocculation monitor is a Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK), the principles of which have been given by Gregory and Nelson.²⁴⁾ Basically, the intensity of narrow beam of light transmitted through a flowing suspension is monitored by a photodetector, the output of which consists of a steady (dc) component and a much smaller fluctuating (ac) component (The ac component arises from random variations in the number of particles in the suspensions and the fact that the sample is continuously being renewed by flow. The fluctuation follows the Poisson distribution, so that the root mean square (rms) value of the fluctuating signal increases markedly as particle aggregation occurs and provides a very sensitive measure of the extent of flocculation).²⁵⁾

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 ($R = \text{rms}/\text{dc}$), because the dc value may change only slightly as flocculation proceeds and the ratio value provides a signal which is largely immune to such problems as electronic drift and fouling of optical surfaces. The output of PDA 2000 was

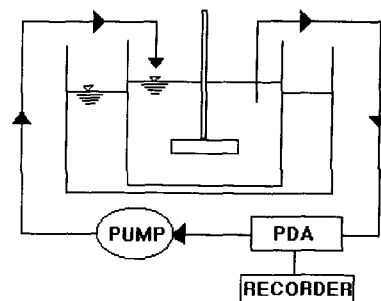


Fig. 1. Flocculation test arrangement.

conveyed to digital form and logged by a chart recorder. The arrangement is systematically shown in Fig. 1.

Zeta potential of humic acid 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).

2.2. Methods

Flocculation tests were carried out in a 300 mL Pyrex beaker with 200 mL of humic acid solutions at a concentration of 25 mg/L containing different kaoline suspensions (0, 15, 35 and 55 NTU), which were placed into a water bath to maintain a constant temperature (20°C). In these cases, the humic acid solutions were adjusted to pH 5, 7 and 9 with 0.1 N HNO₃/NaOH, as described above, in order to examine the effect of pH on flocculation of humic acid by cationic polyelectrolytes. The humic acid solution containing different kaoline suspensions, was adjusted to pH 7 and stirred rapidly with a magnetic stirrer for 24 hrs in order that humic acid may contact sufficiently with kaoline particles. A predetermined amount of each cationic polyelectrolyte was added to the solution or suspension. Immediately after the addition of cationic polyelectrolytes, the solution or suspension was stirred rapidly (200 rpm corresponding to about shear rate 869 s⁻¹) for 1 min, followed by slow stirring (50 rpm corresponding to about shear rate 109 s⁻¹) for 15 min, with a single flat blade (67 mm x 8 mm x 1 mm thick) with a clearance of 10 mm above the base of the beaker. This mixing condition was the optimum in terms of ratio

values which show a sensitive indication of the state of aggregation of the particle. During the stirring, ratio values were logged for analysis. Immediately after flocculation test, 25 mL of the solution or 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 ranged around 5% of the mean, or less. The other solution or suspension was centrifugated at 4000 rpm for 20 min, and the supernatant liquid was taken and used for the absorbance at 254 nm, in order to examine the removal efficiency of humic acid with the dosage of cationic polyelectrolytes. For the humic acid solution containing kaoline suspensions, the residual turbidity was also measured by settling the suspension for 2 hrs and taking the suspension below 2 cm from the surface by a pipette.

3. Results and Discussion

3.1. Effect of polyelectrolyte dosage

When different amounts of cationic poly-

electrolytes were added to the humic acid solution (25 mg/L), the monitor response was shown in Fig. 2. The ratio (rms/dc) value, R, was monitored for 16 min after polyelectrolyte addition. Since this value is a sensitive indication of the state of aggregation of the particle, it is termed Flocculation Index (FI). It is reported that the flocculation curve can be arbitrarily divided into 4 regions^{25,26}: region A (where there is little change in FI value with time), region B (where FI value shows a distinct rise as flocculation begins), region C (where the flocculation rate has become constant and FI value shows a nearly linear rate of increase), and region D (where there is a levelling-off of the FI value). For P-A, the value of FI shows essentially no change at the lowest dosage (22.5 mg/L), indicating little or no flocculation in 16 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 steeper, indicating more rapid flocculation. In this case, the optimum dosage appears to be 29.0 mg/L, where the slope is the steepest and the maxi-

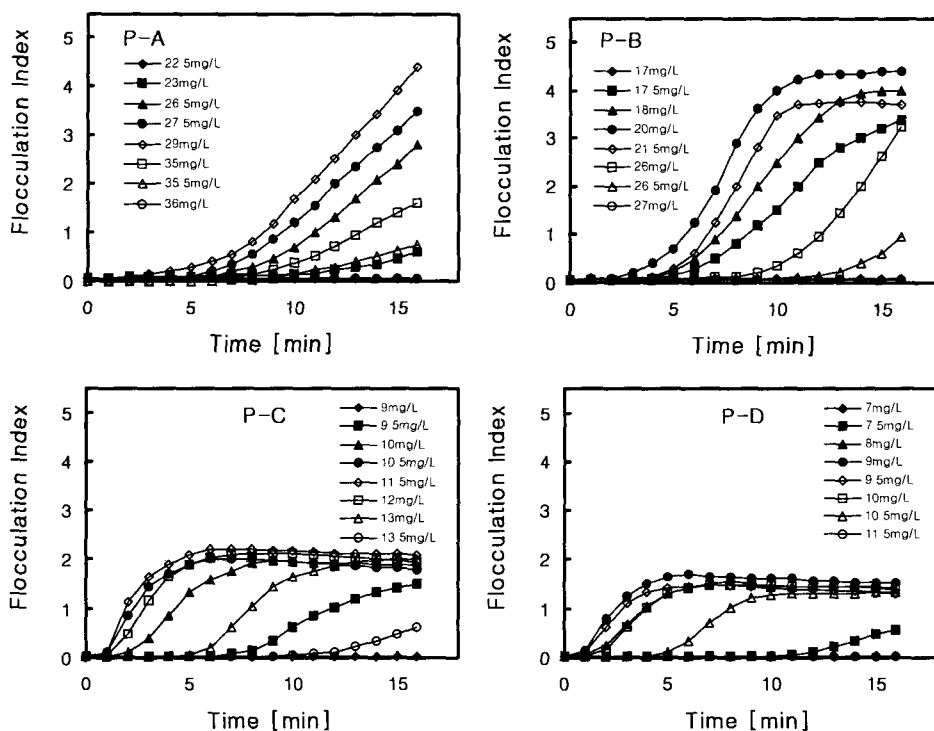


Fig. 2. The effect of polyelectrolyte dosage on flocculation of humic acid (25 mg/L, pH 7).

imum 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 humic acid solution rapidly acquire excess polyelectrolyte so that the collision efficiency is reduced because of restabilization. At the highest dosage (36.0 mg/L), the FI value also shows little change like as at the lowest dosage (22.5 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 similar molecular weight, it can be shown that smaller 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. It is estimated that by the results that electrostatic repulsion between polyelectrolyte segments becomes more significant at the higher charge density and this leads to a greater expansion of the 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 29.0 mg/L, 20.0 mg/L, 11.5 mg/L and 9.0 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 similar 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.

At the optimum dosage, the flocculation began at about 3 min, 2 min, 1 min and 1 min for P-A, P-B, P-C and P-D, respectively, and the maximum FI value was obtained at about 10 min, 5 min and 5 min for P-B, P-C and P-D, respectively. However, for P-A, it was not obtained within 16 min investigated in this study, indicating that the flocculation was in progress. From these results, it can be concluded that for the polyelectrolytes of higher charge density, a shorter time is required to destabilize the humic acid solution, the flocculation occurs rapidly, and less dosage is needed to acquire an optimum flocculation.

The residual fraction of humic acid with polyelectrolyte dosage was obtained by the centrifugation after flocculation test (Fig. 3). It was measured as the absorbance ratio at 254 nm between the residual and initial humic acid concentrations. As shown in Fig. 3, its residual fraction with the amount dosed, changes sharply for the polyelectrolytes of higher charge density, but changes rather broadly for those of lower charge density. Also it can be shown that the maximum removal efficiency of humic acid is obtained at the optimum dosage of each polyelectrolyte and is higher for polyelectrolytes of higher charge density (Fig. 4), pointing out the importance of charge neutralization. This conclusion is reinforced by the zeta potential data (Fig. 5). Reversal of the humic charge

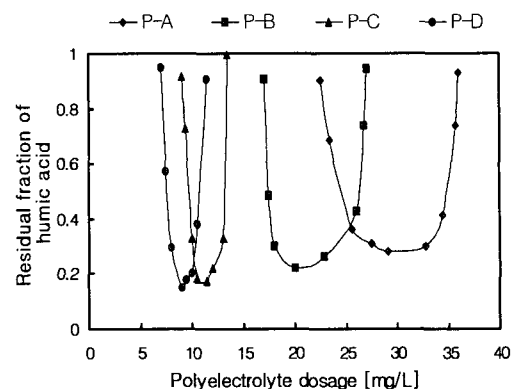


Fig. 3. Residual fraction of humic acid by centrifugation after flocculation test with the dosage of each polyelectrolyte (initial humic acid conc.: 25 mg/L, pH 7).

from negative to positive, occurs at a certain polyelectrolyte dosage, which is close to the optimum flocculation dosage, i.e., at the optimum dosage of each polyelectrolyte, the charge

of humic acid flocculated approaches to near zero.

3.2. Effect of kaoline particles

The effect of kaoline particles (15, 35 and 55 NTU) on the flocculation of humic acid solution (25 mg/L, pH 7) by cationic polyelectrolytes were investigated (Fig. 6). The optimum

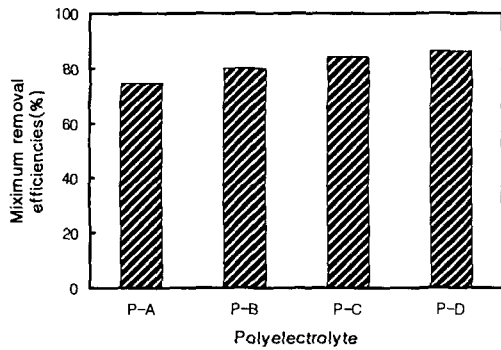


Fig. 4. Maximum removal efficiency of humic acid by each polyelectrolyte (initial humic acid conc.: 25 mg/L, pH 7). This was obtained at the optimum dosage of each polyelectrolyte (P-A: 29.0 mg/L, P-B: 20.0 mg/L, P-C: 11.5 mg/L, P-D: 9.0 mg/L).

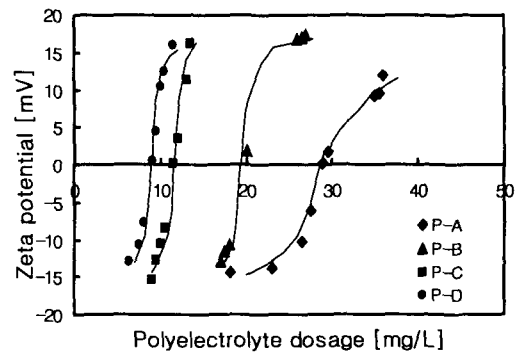


Fig. 5. Zeta potential of humic acid (25 mg/L, pH 7), flocculated with the dosage of each polyelectrolyte.

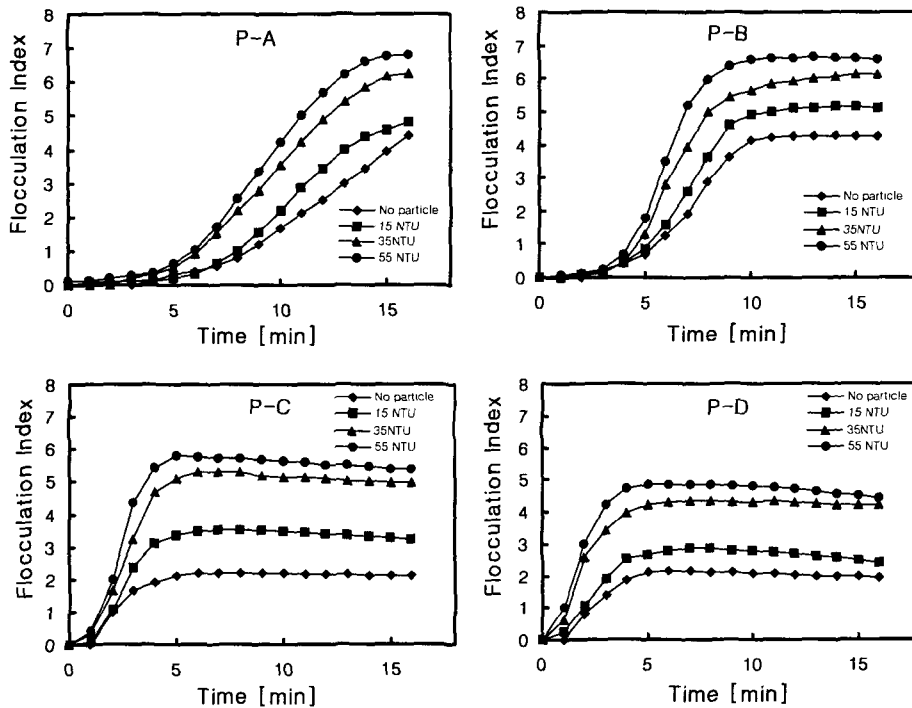


Fig. 6. Effect of kaoline particles of different turbidity (15, 35 and 55 NTU) on flocculation of humic acid (25 mg/L, pH 7) at the optimum dosage of each cationic polyelectrolyte.

flocculation in this case, was observed at the same dosage as the optimum dosage of each polyelectrolyte (P-A: 29.0 mg/L, P-B: 20.0 mg/L, P-C: 11.5 mg/L, P-D: 9.0 mg/L) in the absence of kaoline particles, and the dosages were the same, regardless of kaoline turbidity used in this study. It is considered that the reason for this is caused by the fact that a much smaller dosage is required to obtain an optimum flocculation for the kaoline particles, as compared to the optimum dosage needed for humic acid concentration used in this study. It was reported in previous research that the optimum flocculation for the kaoline particles used in this study was found at the dosage of 0.75 mg/L, 0.40 mg/L, 0.05 mg/L and 0.04 mg/L for P-A, P-B, P-C and P-D, respectively, regardless of kaoline turbidity.²⁶⁾ However, it can be seen that with increasing kaoline content, the lag phase reduces and the slope in region C becomes steeper, leading to a higher FI value. It is considered that this result is ascribed to the fact that kaoline particles act as nucleation sites for the formation of larger flocs. Based on this assumption, it is expected that the humic acid flocculated by cationic polyelectrolytes in the presence of kaoline particles can be settled more rapidly than that in the absence of kaoline particles.

The maximum removal efficiency of kaoline particles with different turbidity in this case was shown in Fig. 7. It can be shown 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.

The change in zeta potential of humic acid in the presence of kaoline particles of different turbidity was examined after flocculation test for 16 min over a range of polyelectrolyte dosage. The effect of kaoline particles with 35 NTU on the zeta potential of humic acid flocculated by each cationic polyelectrolyte was shown in Fig. 8. For the kaoline particles of different turbidity (15 and 55 NTU), the same results were obtained. It can be shown that the zeta potential of humic acid in the presence of kaoline particles approaches to near zero at the optimum dosage of each polyelectrolyte, as in the absence of kaoline particles. From the results obtained in section 3-1 and this section, 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 humic acid.

3.3. Effect of pH

It has been reported that the pH of the solution also affects the flocculation of organic matter.^{27,28)} In order to examine the effect of pH on flocculation of humic acid (25 mg/L) by

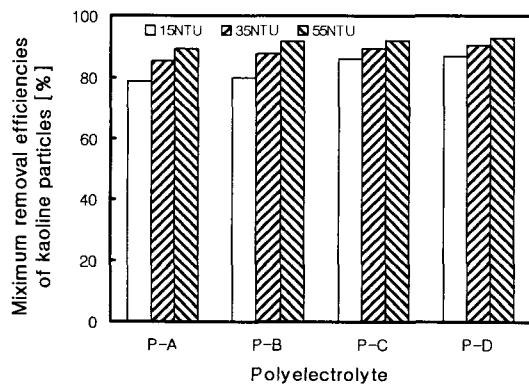


Fig. 7. Maximum removal efficiency of kaoline particles of different turbidity by each polyelectrolyte. This was obtained by settling for 2 hrs after flocculation test for humic acid in the presence of kaoline particles at the optimum dosage of each polyelectrolyte (P-A: 29.0mg/L, P-B: 20.0 mg/L, P-C: 11.5 mg/L, P-D: 9.0 mg/L).

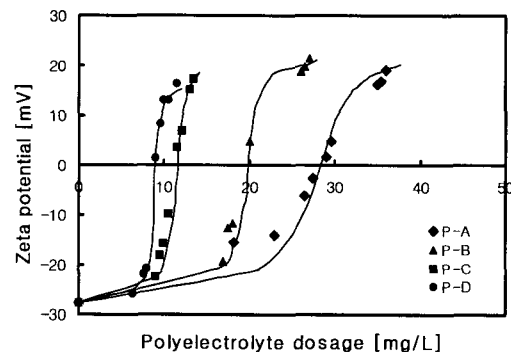


Fig. 8. Zeta potential of humic acid (25 mg/L, pH 7) in the presence of kaoline particles (35 NTU), flocculated with the dosage of each polyelectrolyte.

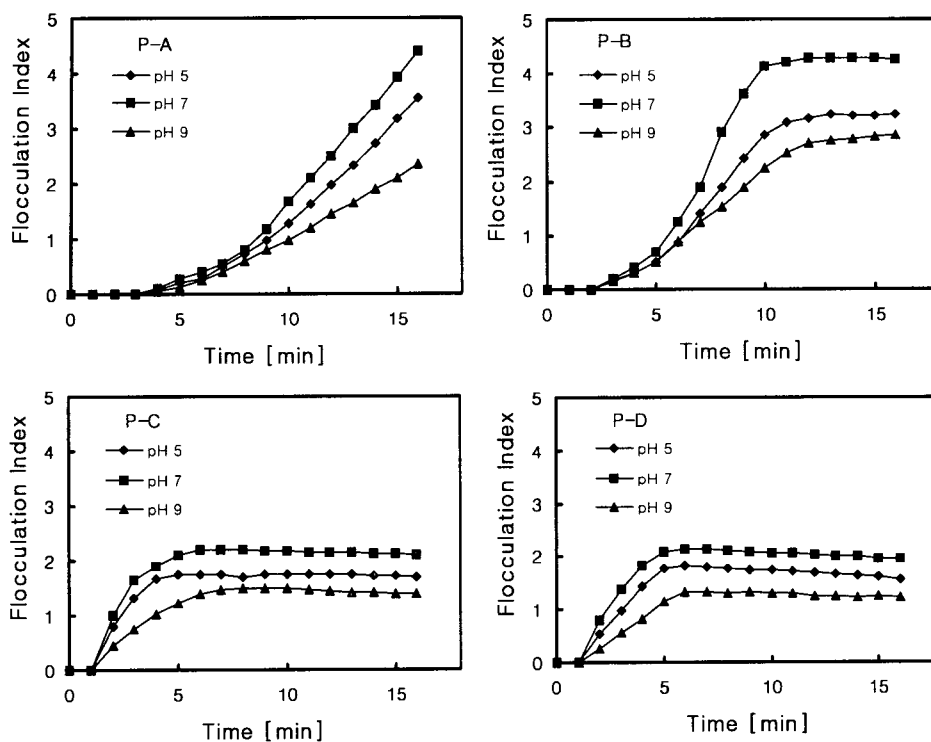


Fig. 9. Effect of pH on flocculation of humic acid (25 mg/L, pH 7) at the optimum dosage of each cationic polyelectrolyte. The optimum dosages obtained at pH 5, 7 and 9 are as follows: 25.0 mg/L, 29.0 mg/L and 31.0 mg/L for P-A, 17.0 mg/L, 20.0 mg/L and 22.0 mg/L for P-B, 10.5 mg/L, 11.5 mg/L and 12.0 mg/L for P-C, and 7.5 mg/L, 9.0 mg/L and 9.5 mg/L for P-D, respectively.

cationic polyelectrolytes, the humic acid solution was adjusted to pH 5, 7 and 9 with 0.1 N HNO_3/NaOH , then the flocculation test was carried out in a wide range of polyelectrolyte dosage. The optimum dosages obtained at pH 5, 7 and 9 in the same way as above, were 25.0 mg/L, 29.0 mg/L and 31.0 mg/L for P-A, 17.0 mg/L, 20.0 mg/L and 22.0 mg/L for P-B, 10.5 mg/L, 11.5 mg/L and 12.0 mg/L for P-C, and 7.5 mg/L, 9.0 mg/L and 9.5 mg/L for P-D, respectively. It is considered that the reason why the optimum dosage increases with increasing pH is ascribed to the increase of negatively charged groups of humic acid¹¹⁾ and/or the partial hydrolysis of the polyelectrolytes.¹⁷⁾

The flocculation curves obtained with pH at the optimum dosage of each polyelectrolyte were shown in Fig. 9. The FI values decreased in the order of pH 7 > pH 5 > pH 9, regardless of the polyelectrolytes used in this study. Also,

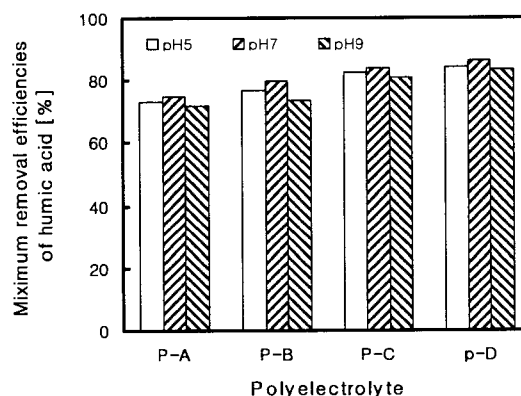


Fig. 10. Maximum removal efficiency of humic acid obtained at the optimum dosage of each cationic polyelectrolyte. The dosages are referred in Fig. 9.

the maximum removal efficiency of humic acid obtained by centrifugation after the flocculation test for 16 min, was the same order as pH

(Fig. 10). For the present being, it may be difficult to explain this phenomenon, although several factors including the partial hydrolysis of polyelectrolytes are connected to the results. More detailed studies, such as the physical and chemical properties of the polyelectrolytes, and their interactions with anionic polyelectrolytes, and others, are needed to explain this phenomenon.

4. Conclusions

The effects of polyelectrolyte dosage, kaoline particles of different content and pH on flocculation of humic acid by several cationic polyelectrolytes were investigated using a simple monitoring technique. The method gives useful insight into the behavior of polyelectrolyte flocculants in stirred 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 for the polyelectrolytes of higher charge density, the lag time (the time between the addition of a polyelectrolyte and the onset of flocculation) is shorter, the flocculation occurs more rapidly, less dosage is required to acquire an optimum flocculation, and higher removal of humic acid is obtained at the optimum dosage (where the maximum removal of humic acid is obtained), pointing out the importance of charge neutralization.

It has been found that the optimum dosages are the same regardless of the presence of kaoline particles of different turbidity, but at the dosage, the higher FI values are obtained with increasing kaoline turbidity, which is considered to be due to the formation of larger flocs by the act of kaoline particles as nuclei. Also, it can be shown that the zeta potential of humic acid approaches to near zero at the dosage, regardless of the presence of kaoline particles.

It has been observed that the optimum dosage increases with increasing pH of the humic solution, based on the increase of negatively charged groups of the solution and partial hydrolysis of the polyelectrolytes, etc. and the FI values decrease in the order of $\text{pH } 7 > \text{pH } 5 > \text{pH } 9$, regardless of the polyelectrolytes. More detailed studies are needed to explain the

phenomenon for the latter.

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