

Formation, Breakage and Reformation of Humic Floccs by Inorganic and Organic Coagulants

Sang-Kyu Kam, Min-Gyu Lee*, Kyung-Ho Kang and Mei-Lan Xu

Division of Civil and Environmental Engineering, Cheju National University, Jeju 690-756, Korea

**Division of Applied Chemical Engineering, Pukyong National University, Busan 608-739, Korea*

(Manuscript received 3 December, 2007; accepted 31 December, 2007)

Abstract

The floc formation, breakage and reformation of humic acid by inorganic (alum and PAC) and organic coagulants (cationic polyelectrolytes) at several conditions (pH, ionic strength and floc breakage time) were examined and compared among the coagulants at different conditions using a continuous optical monitoring method, with controlled mixing and stirring conditions. For alum, the shapes of formation, breakage and reformation curves at different pH (5 and 7) were different, but the shapes and the sizes of initial floc and reformed floc were nearly the same in the absence and presence of electrolytes at pH 7. For PAC, similar shapes of the curves were obtained at different pH and ionic strength, but the sizes were different, except for those of reformed floccs at different pH. However, for these coagulants, reformed floccs after floc breakage, occurred irreversibly for all the conditions used in this study. For organic coagulants, the time to attain the initial plateau floc size, the extent of floc strength at high shear rate and reversibility of reformed floccs were different, depending on floc formation mechanism. Especially, for the cationic polyelectrolyte forming humic floccs by charge neutralization or electrostatic patch effect mechanism, reformed floccs occurred reversibly, regardless of pH and floc breakage time, but occurred irreversibly in the presence of electrolytes.

Key Words : Floc breakage, Floc strength, Floc recovery, Humic acid, Inorganic and organic coagulants, Monitoring

1. Introduction

Humic substances which are major components of dissolved organic matter in natural waters, 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^{1,2}. Since their presence in water makes unacceptable for drinking purposes because of undesirable color and the formation of carcinogenic, mutagenic and genotoxic by-products during chlorination^{3,4}, they should be removed during

water treatment.

Several methods are used to remove humic materials in water and a very common method is coagulation/flocculation, followed by either filtration, sedimentation or flotation. Their removal by coagulation/flocculation method greatly depends on the performance of the coagulant and the production of floccs with suitable properties. In stirred tanks, floccs grow initially at a rate that is determined by the applied shear, the concentration of humic materials and the collision efficiency of formed-particles. As floccs become larger, further growth is restricted by the applied shear^{5,6}. A dynamic balance between floc growth and breakage can lead to a steady-state floc size distribution, where the limiting size is dependent on the applied shear rate⁷. However, in other cases a maximum floc size is reached, fol-

Corresponding Author : Sang-Kyu Kam, Division of Civil and Environmental Engineering, Cheju National University, Jeju 690-756, Korea
Phone: +82-64-754-3444
E-mail: sakyukam@cheju.ac.kr

lowed by a decrease, even under the same agitation conditions⁸). It is generally found that flocs become more compact as a result of applied shear⁹. Floc size and structure are of great importance in influencing solids removal efficiency during impurity separation.

When pre-formed flocs are subjected to an increased shear rate, breakage can occur. Breakage depends greatly on the intensity of shear and floc strength. Floc strength is dependent upon the inter-particle bonds between the components of the aggregate¹⁰. Increased floc compaction is considered to increase floc strength due to an increase in the number of bonds holding the aggregate together¹¹.

In water treatment applications, coagulants based on hydrolyzing metal salts, which are commonly used, are rapidly hydrolyzed to form cationic hydroxide species and hydroxide precipitate, depending on pH of the solution and their dosages. Cationic hydroxide species interacts with anionic impurities in water to form insoluble charge-neutral products (charge neutralization). Metal hydroxide precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and, hence, a high probability of capturing impurities. This mechanism has become known as sweep flocculation since impurities in water are swept out of water by an amorphous hydroxide precipitate¹². There have been many previous studies of floc formation and breakage with hydrolyzing metal salts^{13,14}. These have been shown that stirring conditions have a very significant influence on floc growth. When they are subjected to a higher shear rate, flocs undergo breakage. On restoring the previous low shear conditions, flocs can grow back to the previous size, or breakage may be irreversible to some extent¹⁵.

Organic coagulants, such as cationic polyelectrolytes, promote larger flocs and increase the sedimentation velocity dramatically in stirred suspensions¹⁶. Aggregates formed using cationic polyelectrolytes appear to be significantly more resistant to breakage¹⁷. The effectiveness of these coagulants is largely the result of the production of strong flocs by the mechanisms of polyelectrolyte bridging or electrostatic patch effects¹⁸.

The studies on floc formation and breakage have

been carried out with clay particles at fixed conditions without considering floc formation mechanisms. Moreover, it has been reported that ionic strength has an influence on flocculation characteristics of humic acid in previous paper¹⁹. By using standard mixing and stirring conditions, a cycled shear routine and a continuous monitoring method, it is relatively easy to examine the effect of shear conditions on floc formation and break-up. The purpose of this study is to investigate systematically the formation, breakage and reformation of flocs formed with humic acid using inorganic and organic coagulants at several conditions. The characteristics of humic flocs produced by a cycled-shear procedure are compared among the coagulants at different conditions.

2. Materials and Methods

2.1. Materials and apparatus

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

The coagulants used were inorganic (aluminum sulfate (alum), polyaluminum chloride (PAC)) and organic (cationic polyelectrolytes) ones. A stock alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, BDH Co., UK) solution was prepared at a concentration of 1,000 mg Al/L. PAC (Summit Research Lab, USA) had a degree of neutralization, $r(=\text{OH}/\text{Al})$, of 1.7, and was supplied as a 10.2% Al_2O_3 solution. A stock PAC solution was prepared at a concentration of 100 mg Al/L. To prevent ageing effects of these stock solutions, fresh stock solutions were prepared for a sequence of experiments or renewed every two weeks. The stock solutions were kept in a refrigerator at 4°C. Cationic polyelectrolytes used were commercial products, supplied by Ciba Speciality Chemicals, UK. These were poly(diallyldimethylammonium chloride) (P-A) and copolymers of acrylamide and dimethylaminoethyl acrylate (the latter being quaternized with methyl chloride) (P-B and P-C). P-A (a 40% active solution) was prepared as 0.1% aqueous solutions by diluting the products supplied with water. P-B and P-C were supplied as solids and were also 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. All of the 0.1% solutions were used within one week of preparation. The properties of the polyelectrolytes used are given in Table 1.

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 diluting 5 mL of this stock solution and 5 mL of 0.1 N Na_2CO_3 to 1 L to with water. The Na_2CO_3 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 μm cellulose nitrate membrane and adjusted to pH 5 and 7 with 0.1 N or 0.01 N HNO_3/NaOH .

Flocculation monitor is a Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK), which provides a very sensitive measure of the extent of flocculation continuously¹⁶. For dynamic monitoring, a sample from one beaker was circulated through transparent PVC tubing of 2.65 mm internal diameter, by means of a microtube pump (Eyla MP-3N). The pump was located after the PDA instrument to avoid the effects of possible floc breakage in the pinch portion of the pump. The tubing was clamped in the PDA instrument so that the following sample was illuminated by a narrow light beam. The PDA 2000 measures the average transmitted light intensity (dc value) and the root mean square (rms) value of the fluctuating component. The ratio (rms/dc) provides a sensitive measure of particle aggregation¹⁶. In this study, the ratio value is called the flocculation Index (FI). The FI

value is strongly correlated with floc size and always increases as flocs grow larger²². Although it is not possible to derive quantitative information on floc size in this system, the FI value provides a very useful relative indication of floc growth, breakage and regrowth, and allows comparisons to be made between different coagulants and under different experimental conditions.

2.2. Methods

For flocculation tests 800 mL of humic acid solutions (25 mg/L) containing different concentrations (0, 1.0 mM) of electrolytes (NaCl , CaCl_2) were placed in a 1 L Pyrex beaker, which was maintained at a constant temperature (20°C) in a water bath. In these cases, the humic acid solutions were adjusted to pH 5 or 7 with 0.1 N HNO_3/NaOH .

For dynamic tests, the sample was pumped from a stirred beaker at a rate of 15 mL/min through the tubing and the average (dc) and fluctuating (rms) components of the transmitted light intensity were monitored by the PDA instrument. Readings were taken every 2 sec and the results were stored in a computer for subsequent spreadsheet analysis (Fig. 1). Flocculation tests were carried as follows. After the addition of pre-determined amount of each coagulant, the humic acid solution was stirred rapidly (400 rpm corresponding to about shear rate 1156 s^{-1}) for 10 sec, followed by slow stirring (50 rpm corresponding to about shear rate 51 s^{-1}) for 10-25 min, with a single flat blade (65 mm x 29 mm x 1 mm thick) with a clearance of 25 mm above the base of the beaker. Immediately after flocculation test, the zeta potential of flocculated material and residual humic acid concentration with the dosage

Table 1. Properties of cationic polyelectrolytes used

Polyelectrolyte	% Cationic (Charge density, meq/g ^a)	Molecular Weight ^b
P-A	100 (6.20)	$3\text{-}4 \times 10^4$
P-B	20 (0.83)	$2\text{-}3 \times 10^6$
P-C	40 (1.73)	$2\text{-}3 \times 10^6$

^adetermined by spectrophotometry²⁰; ^bcalculated 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 Kulicke²¹.

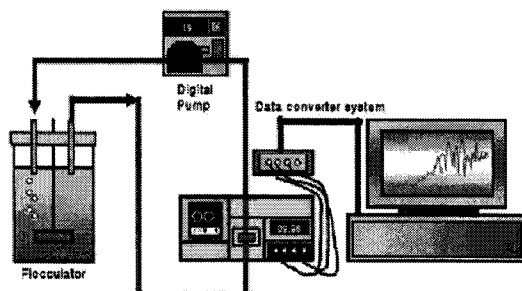


Fig. 1. Schematic diagram of experimental set-up.

of each coagulant were measured. From above results and the FI values, the optimum dosage of each coagulant was determined at different conditions^{19,23}. In order to examine the floc breakage and reformation, an optimum dosage of each coagulant was chosen. The dynamic test was repeated by increasing the stirring speed to 400 rpm for times ranging from 10 to 300 s (to about 15 min for P-B and P-C) after each slow stirring period, and then reduced back to 50 rpm for about 10-15 min, except for P-B and P-C. All experiments were carried out two or three times and very little variation was observed.

3. Results and Discussions

3.1. Dynamic flocculation tests of humic acid among the coagulants

In order to examine the formation, breakage and reformation of humic flocs by the coagulants used in this study, dynamic flocculation tests were conducted. Initially, after the optimum dosage was added to 800 mL of humic acid solution (25 mg/L, pH 7), it was stirred at 400 rpm for 10 sec, followed by slow stirring at 50 rpm for 10-25 min depending on the coagulants (i.e., depending on the coagulants, the time required to arrive at the maximum FI value was different). For dynamic tests of floc breakage and reformation, the stirring rate was increased to 400 rpm for 30 sec (for about 15 min for P-B and P-C) after the slow stirring period, and then reduced back to 50 rpm for about 10-15 min, except for P-B and P-C. The optimum dosage of each coagulant was determined from zeta poten-

tial measurement, residual humic acid concentration and the FI value with the dosage as described in the section 2.2 and was 13.7 mg Al/L for alum, 2.3 mg Al/L for PAC, 9 mg/L for P-A, 29 mg/L for P-B and 20 mg/L for P-C. The results are shown in Fig. 2.

Fig. 2(a) shows the results for inorganic coagulants (alum and PAC). A region of constant FI (or floc size) was reached rather quickly (at about 200 sec) for these coagulants, which is generally thought to reflect a rapid balance between floc growth and breakage under this experimental condition, although the flocculation mechanism of humic acid is different depending on the alum and PAC at pH 7 (i.e., its flocculation occurs by sweep flocculation mechanism for alum and by charge neutralization mechanism for PAC)¹⁹. From this result, it is believed that the flocculation of humic acid at pH 7 begins soon after coagulant dosing due to a rapid hydroxide precipitation for alum and due to a high charge density for PAC. However, the initial plateau value of the FI for alum is higher (about 2 times) than PAC, indicating that larger (and hence stronger) floc for the former is formed than for the latter. The floc breakage was rather rapid with 30 sec breakage period, as shown by a rather sharp fall in the FI value as soon as the stirring speed is increased to 400 rpm, regardless of these inorganic coagulants. On returning to the slow stirring speed (50 rpm) for these coagulants, some floc regrowth occurred, but the FI values reached only a fraction of the previous value. The new plateau value was much lower than the first value, and reached more slowly, indicating that the breakage of humic flocs

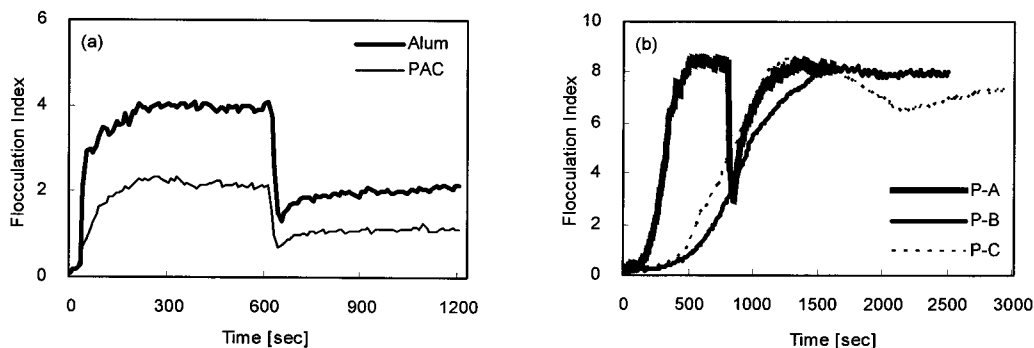


Fig. 2. Formation, breakage and reformation of humic flocs by inorganic (a) and organic coagulants (b) at pH 7.

formed by these inorganic coagulants under the stated conditions is irreversible. Although the reason why these inorganic coagulants show the irreversible nature of floc breakage remains unclear, it may be that floc breakage involves cleavage of chemical bonds in the precipitated hydroxide (for alum) and hydrolyzed polymeric aluminum species (for PAC), followed by rearrangement to give less reactive sites.

Fig. 2(b) shows the results for organic coagulants (P-A, P-B and P-C). In these cases, the onset of flocculation occurred rather later than for the inorganic coagulants and longer times were needed to attain the plateau FI value, especially with P-B and P-C. It is considered that the lag time for these organic coagulants is due to the relatively slow adsorption of these materials on the humic acid. However, the final FI values were much higher, indicating larger flocs.

P-A promoted the growth of large flocs, with FI value about two times higher than alum and similar to that for the other organic coagulants (P-B and P-C), together with a more rapid onset of flocculation among the organic coagulants. The finding that the floc size for P-A is similar to that for P-B and P-C is difficult to explain in terms of the different molecular weights, since it is expected that higher molecular weight polyelectrolyte gives a stronger floc as a result of polyelectrolyte bridging effect²⁴. This point will be investigated in more detail in the next study. P-A shows a shorter lag time (about 2 min) and a shorter time to reach a maximum FI value (about 10 min), which may be a result of its more rapid diffusion due to the low molecular weight²⁵ and a greater collision radius due to a greater expansion between polyelectrolyte segments with high charge density²³ than the much higher molecular weight and lower charged P-B and P-C. Breakage at 400 rpm was rapid and gave about three-fold reduction in FI. Regrowth of floc at 50 rpm was substantial and the final FI reached the same value as that before breakage, indicating that regrowth at 50 rpm after floc breakage occurs reversibly differently from inorganic coagulants.

When P-B or P-C was used as the coagulant, the plateau FI value was similar to that for P-A, as mentioned above. However, the behaviors for floc breakage

at 400 rpm and floc regrowth at 50 rpm after floc breakage was different from P-A. These coagulants form the humic flocs by the mechanisms of polymeric bridging based on their high molecular weight and charge neutralization (or electrostatic patch) based on their charge density²³. Differently from P-A, the breakage of humic flocs formed by these coagulants did not occur at 400 rpm during the short breakage time (30 sec) applied by the other coagulants. At a rather longer breakage time (about 15 min), it did not occur for P-B and occurred slightly for P-C, indicating that P-B with low charge density forms a stronger humic floc than P-C with high charge density, although these coagulants have the same high molecular weight. This result is the same as that the stronger flocs were produced for the polyelectrolytes with the charge density in the range of 0.18-1.42 meq/g than those with the charge density below 0.18 meq/g and above 1.42 meq/g in the study of the effect of polyelectrolyte charge density on sewage floc strength for high molecular weight, cationic polyelectrolytes²⁶. As shown in Table 1, the charge densities of P-B and P-C determined by spectrophotometry were 0.83 and 1.73 meq/g, respectively. The reason for the production of a stronger floc for P-B than P-C is assumed to be related to the flocculation mechanism for the floc formation. When the polyelectrolytes with high molecular weight have high charge density, they adopt a flatter configuration on the surface of humic acid when adsorbed, and so there is less scope for bridging between humic acids. Flocculation then occurs because of electrostatic attraction between positively charged polyelectrolytes adsorbed on one humic acid and negatively charged areas on other humic acid (electrostatic patch mechanism). Thus, it is considered that although P-B and P-C produce humic flocs by both polymeric bridging and electrostatic patch mechanism, P-B produce humic floc via a polyelectrolyte bridging mechanism rather than an electrostatic patch mechanism compared with P-C²⁷, resulting in stronger flocs than P-C. The regrowth at 50 rpm after floc breakage for P-C did not occur reversibly differently from P-A, which is considered to be due to the scission of polyelectrolyte chains under this high shear rate²⁸ and adoption of a more flat config-

uration by adsorbed polyelectrolyte during the breakage phase²⁵).

As shown above, P-B and P-C produce stronger humic flocs which are not readily broken under the experimental conditions given for the other coagulants, making the comparison of floc characteristics with those difficult. Thus, the characteristics of floc breakage and reformation in the following sections were examined for the other coagulants (alum, PAC, P-A) except for P-B and P-C.

3.2. Effect of pH

It is well-known that the pH of the solution or suspension affects the flocculation characteristics of organic matter or particles by the coagulants^{19,29}. In order to examine the effect of pH on the characteristics of humic flocs by inorganic (alum, PAC) and organic (P-A), the optimum dosage of each of the coagulants was added to 800 mL of humic acid solution (25 mg/L) adjusted to pH 5 and 7, and carried out according to the experimental methods at 30 sec breakage period. The optimum dosages determined were 3.9 mg Al/L (pH 5) and 13.7 mg Al/L (pH 7) for alum, 1.1 mg Al/L (pH 5) and 2.3 mg Al/L (pH 7) for PAC, and 7.5 mg/L (pH 5) and 9 mg/L (pH 7) for P-A. It is considered that the increase of each coagulant dosage with increasing pH is mainly ascribed to the increase of negatively charged groups of humic acid³⁰. The results are shown in Fig. 3.

Fig. 3(a) shows the results for alum at pH 5 and 7. It can be found that the shapes of formation, breakage and reformation curves for alum at pH 5 and 7 are different, indicating that the flocculation of humic

acid by alum at each pH occurs by different mechanism (i.e., its flocculation occurs by charge neutralization mechanism at pH 5 and by sweep flocculation mechanism at pH 7)¹⁹. At pH 7, the time to reach an initial plateau value of the FI was shorter and the FI value was higher than at pH 5, revealing that for alum, a more rapid and stronger humic floc is produced by sweep flocculation mechanism than by charge neutralization mechanism. The floc breakage was rather rapid as soon as the stirring speed was increased to 400 rpm for 30 sec, regardless of flocs produced by different mechanisms. On returning to the slow stirring (50 rpm), the FI values reached only a fraction of the previous value, indicating that the breakage of humic flocs formed by alum is irreversible, regardless of flocs produced by different mechanisms. However, the new plateau value at pH 5 was higher than that at pH 7. It was discussed briefly in section 3.1 for the irreversible nature of floc breakage in case of humic floc produced by sweep flocculation at pH 7 for alum, although the underlying mechanisms remain unclear. When the interaction between humic acid is of a physical nature (such as van der Waals or electrostatic attraction), there is no obvious reason why aggregates should not reform after breakage. Although it is difficult to explain the reason why reformed flocs shows the irreversibility in case of floc produced by charge neutralization at pH 5 for alum, it is estimated that the reformed floc may have a different (more compact) structure than before breakage.

Fig. 3(b) shows the results for PAC at pH 5 and 7. The shapes of formation, breakage and reformation

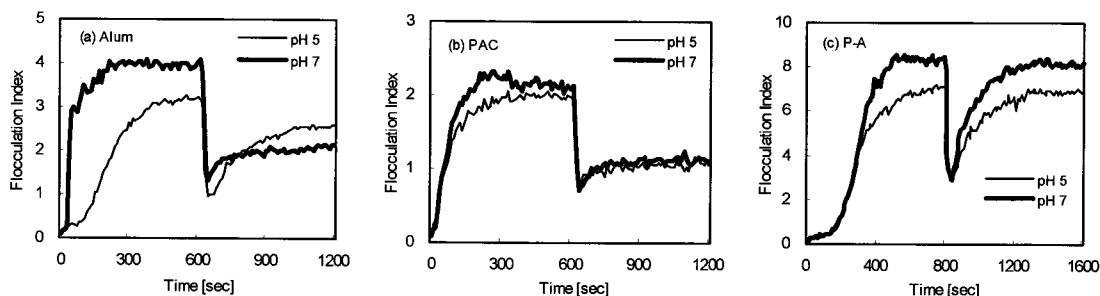


Fig. 3. Effect of pH (5, 7) on the formation, breakage and reformation on the humic flocs by alum (a), PAC (b) and P-A (c).

curves at pH 5 and 7 were nearly the same differently from alum, indicating that the flocculation of humic acid by PAC at each pH occurs by same mechanism (i.e., its flocculation occurs by charge neutralization mechanism at pH 5 and 7)¹⁹. The initial plateau value at pH 7 was a little higher than that at pH 5, which is considered that a little larger floc is formed by the increase of the dosage with increasing pH. However, the FI values for the broken floc at 400 rpm for 30 sec and reformed floc at slow stirring at 50 rpm were nearly the same at pH 5 and 7, indicating that pH has no effect on those and so floc breakage is irreversible regardless of pH, by presumably the cleavage of chemical bonds in the hydrolyzed polymeric aluminum species as described in section 3.1.

When P-A was used as the coagulant, similar shapes of formation, breakage and reformation curves at pH 5 and 7 were obtained (Fig. 3(c)) likewise for PAC, indicating that the flocculation of humic acid by P-A at each pH occurs by same mechanism. The initial plateau value at pH 7 was a little higher than that at pH 5 likewise for PAC, due to the formation of a little larger floes by the increase of the dosage with increasing pH. However, the plateau value of the FI for reformed floc at each pH was nearly the same, differently from PAC, indicating that regrowth at 50 rpm after floc breakage occurs reversibly regardless of pH.

3.3. Effect of ionic strength

The ionic strength of the solution can affect the flocculation of impurities in water in several ways^{19,20}. The electrolytes in water can also destabilize the impurities by reduction of electrical repulsion among the charged impurities, and so less coagulant dosage is needed to bring about flocculation in case that they are destabilized by the mechanisms of charge neutralization or electrostatic patch effect. In order to examine the effect of ionic strength on the characteristics of humic floes by inorganic (alum, PAC) and organic (P-A), the optimum dosage of each of the coagulants was added to 800 mL of humic acid solution (25 mg/L, pH 7) containing 1 mM of electrolytes (NaCl, CaCl₂) (which are generally found in natural waters) and carried out according to the experimental methods at 30 sec breakage period and the results were compared

with those in their absence. The optimum dosages determined were 13.7 mg Al/L regardless of electrolytes for alum, 2.3 mg Al/L (NaCl) and 1.7 mg Al/L (CaCl₂) for PAC, and 9 mg/L (NaCl) and 6.5 mg/L (CaCl₂) for P-A. Comparing the optimum dosages of each of the coagulants at pH 7 in the absence (see sections 3.1 and 3.2) and in the presence of 1 mM of NaCl and CaCl₂, they are the same for alum forming the humic floes by sweep flocculation mechanism, but for PAC and P-A forming humic floes by the mechanism of charge neutralization or electrostatic patch effect, they in the case of absence of electrolytes and presence of 1 mM NaCl are the same but are less in the presence of 1 mM CaCl₂, indicating that monovalent cationic species (NaCl) has no effect on the optimum dosage but divalent cationic species (CaCl₂) has an effect on that to some extent. The results are shown in Fig. 4.

Fig. 4(a) shows the results for alum in the absence and presence of 1 mM of electrolytes (NaCl and CaCl₂) at pH 7. The shapes of formation, breakage and reformation curves for alum at pH 7, were nearly the same in the absence and in the presence of different electrolytes, indicating that the electrolytes (1 mM) examined in this study have little effect on the characteristics of humic floes formed by sweep flocculation mechanism.

Fig. 4(b) shows the results for PAC at pH 7. The initial plateau value of the FI in the presence of 1 mM of NaCl or CaCl₂ was a little higher (especially for CaCl₂) than that in the absence of electrolytes, indicating that the floes formed in their presence is a little greater. The floc breakage with 30 sec breakage period was rapid and its shapes were nearly the same, regardless of the absence and presence of electrolytes, although the FI value in the presence of CaCl₂ was a little higher. On returning to the slow stirring (50 rpm) after floc breakage, the reformation of the floes in their presence occurred irreversibly likewise in their absence, but a little larger floes were reformed for the former (especially for CaCl₂) than for the latter, which is considered due to presumably the cleavage of chemical bonds in the hydrolyzed polymeric aluminum species as described in section 3.1 and 3.3, but the formation of floes between the electrolytes and humic

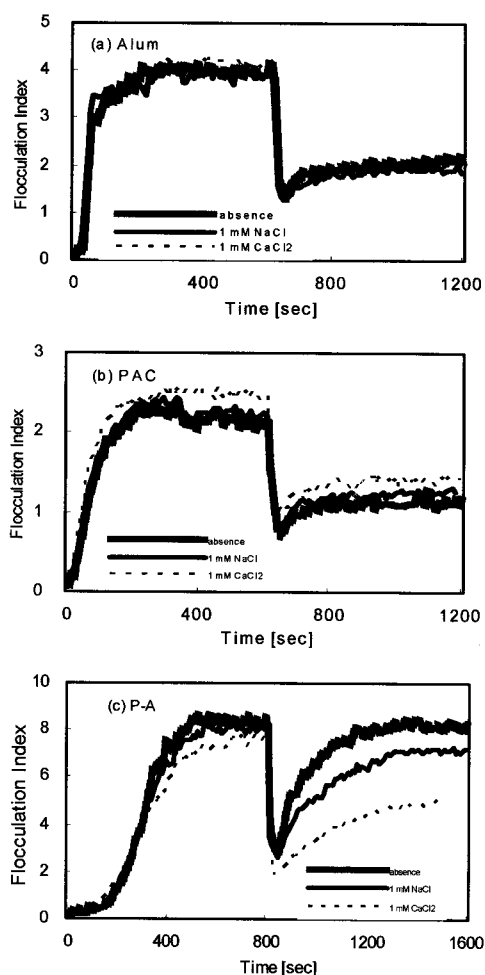


Fig. 4. Effect of ionic strength (1 mM of NaCl and CaCl_2) on the formation, breakage and reformation on the humic flocs by alum (a), PAC (b) and P-A (c).

acid and a little larger flocs between divalent species (CaCl_2) and humic acid.

Fig. 4(c) shows the results for P-A in the presence of 1 mM of electrolytes (NaCl and CaCl_2) and their absence at pH 7. The initial plateau values of the FI in their presence were lower than the value in their absence, which reveals smaller flocs are formed with the results of flocculation between those and humic acid. Especially, in the presence of 1 mM CaCl_2 , less dosage was needed to obtain an optimum flocculation and so much smaller floc was formed with the result of flocculation between this electrolyte and humic, differently

for PAC. The floc breakage with 30 sec breakage period was rapid and its shapes were nearly the same, regardless of their absence and presence. However, the FI values in their presence were lower than the value in their absence, indicating that weaker flocs are formed in their presence than their absence. On returning to the slow stirring (50 rpm), the FI values in their presence reached only a fraction of the previous value, whereas the value in their absence was nearly the same, indicating that the reformed flocs in their presence occur irreversibly. When the humic floc is formed by a physical interaction, there is no obvious reason why aggregates should not reform after breakage, as described for alum at pH 5 in section 3.2. Although it is difficult to explain the reason why reformed flocs in their presence show the irreversibility, it is estimated that the reformed flocs in their presence may have a different structure than before breakage. Especially, in the presence of 1 mM CaCl_2 , the optimum dosage of P-A was reduced and so its effect for reformed floc may be greater than in the presence of 1 mM NaCl, resulting in a greater irreversibility.

3.4. Effect of floc breakage time

Fig. 5 shows the results of flocculation experiments with the same stirring speed during the floc breakage phase (400 rpm), but with different stirring durations (10, 30, 60 and 300 sec) for alum and P-A at pH 7. After the optimum dosage each of the coagulants (13.7 mg Al/L for alum, 9 mg/L for P-A), was added to the humic acid solution (25 mg/L, pH 7), it was stirred at 400 rpm for 10 sec, followed by slow stirring at 50 rpm for 10-15 min. After that, the stirring speed increased to 400 rpm for the different durations, and then reduced back to 50 rpm for 10-15 min again.

Fig. 5(a) shows the results for alum. With the 30 sec and 60 sec breakage periods, the floc breakage gives the similar decrease in FI. In these cases, there is a similar degree of recovery after the stirring speed is reduced to 50 rpm. With only 10 sec at 400 rpm, the FI value shows a smaller decrease, presumably because there is insufficient time to complete the initial breakage. It is noteworthy that there is a greater degree of recovery and that the rise in FI is more rapid than for the longer breakage periods. With 300 sec at 400

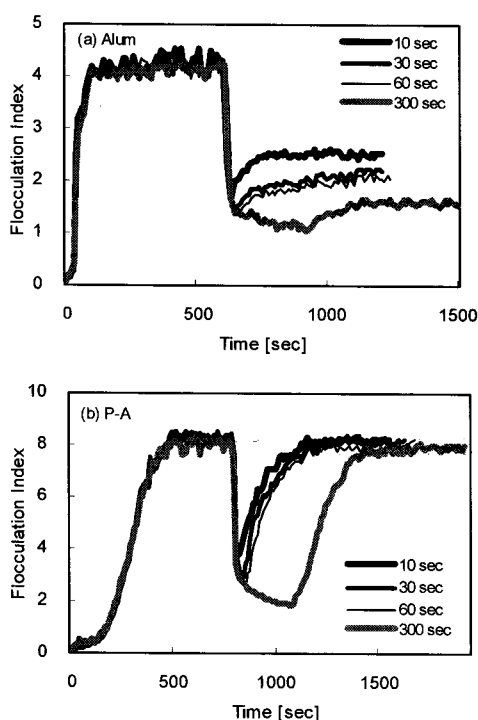


Fig. 5. Breakage of humic floes at 400 rpm with different durations for alum (a) and P-A (b).

rpm, there is evidence of much more gradual decrease in FI with a more limited recovery at 50 rpm. In all cases, the FI values of reformed floes were only a fraction of the previous value, indicating that the breakage of humic floes formed by alum under the stated conditions is irreversible, regardless of floc breakage time. The same results were obtained for PAC, although these are not shown in Fig. 5.

When P-A was used as the coagulant, almost full reversibility of floc breakage was obtained (Fig. 5(b)). Apart from a delay, corresponding to the breakage time, the rate of floc regrowth was about the same in all cases and the FI reached the same value as that before breakage, indicating that the duration of the breakage has no effect on the reformation of the floes, differently from alum and PAC. The results for the effect of floc breakage time for these coagulants was identical in the above sections of this study.

Following Francois¹³, the breakage and regrowth of floes under cycled shear conditions can be quantified

Table 2. Strength and recovery factors obtained for different breakage times at 400 rpm and pH 7 using different coagulants

		Coagulant	10 sec	30 sec	60 sec	300 sec
Strength factor	Alum		39	35	33	25
	PAC		40	34	32	24
	P-A		43	36	34	23
Recovery factor	Alum		33	26	25	19
	PAC		32	26	24	18
	P-A		99	98	98	97

by a breakage factor and a recovery factor, but in terms of Flocculation Index, rather than measured floc size, for initial (FI_1), broken (FI_2) and reformed (FI_3) floes³¹. With this terminology, the two factors (%) can be defined as:

$$\text{Strength factor} = (FI_2/FI_1) \times 100 \quad (1)$$

$$\text{Recovery factor} = [(FI_3-FI_2)/(FI_1-FI_2)] \times 100 \quad (2)$$

Strength and recovery factors obtained for different shear times using different coagulants are given in Table 2. The strength factors at each breakage time for the coagulants are nearly the same. The recovery factors are markedly different for the inorganic and organic coagulants. For the inorganic coagulants, they are in the range of 19-33%, with being nearly the same among the coagulants and decreasing with longer breakage time. However, the floc produced by P-A show the recovery factors of 97% or above, indicating almost complete recovery.

4. Conclusions

The floc formation, breakage and reformation of humic acid by inorganic (alum and PAC) and organic coagulants (P-A, P-B and P-C) at several conditions were investigated using a continuous optical monitoring method, with controlled mixing and stirring conditions.

When an alum was used as the coagulant, the shapes of formation, breakage and reformation curves were different depending pH. The humic floc formed by sweep flocculation mechanism occurred more rapidly, its floc size was greater, but the size of floc reformed at slow stirring was smaller, compared with each corre-

sponding result by charge neutralization mechanism. However, the floc reformed after floc breakage occurred irreversibly, regardless of floc formation mechanism. Under the condition that the humic floc is formed by sweep flocculation mechanism, the electrolytes (1 mM of NaCl, CaCl₂) used in this study did not affect the above shapes and the sizes of initial floc and reformed floc after floc breakage.

For PAC, similar shapes of formation, breakage and reformation curves were obtained, regardless of pH, indicating that the flocculation of humic acid by PAC at each pH occurs by same mechanism (charge neutralization mechanism). The initial humic flocs were formed more rapidly due to its high charge density, regardless of pH, but the floc size at pH 7 was greater than at pH 5 due to the increase of its dosage with increasing pH. The FI values of broken and reformed flocs at pH 5 and 7 were nearly the same and reformed flocs occurred irreversibly, regardless of pH. The initial floc and reformed floc in the presence of electrolytes, were a little greater than those in their absence, with greater floc in the presence of high valent cationic electrolyte.

When the organic coagulants (P-A, P-B and P-C) were used, the onset of flocculation occurred rather later, longer times were needed to attain the plateau FI value, especially with high molecular weight polyelectrolytes (P-B and P-C), but larger flocs were formed, compared with the inorganic coagulants. For P-A, the onset of flocculation occurred more rapidly among the organic coagulants, but its floc size was similar to that for P-B or P-C. Breakage at high shear rate was rapid and regrowth of flocs at slow stirring occurred reversibly differently from inorganic coagulants. However, the sizes of initial floc and reformed floc were smaller at lower pH due to low dosage with decreasing pH. In the presence of electrolytes, the sizes of initial floc and reformed floc were smaller than those in their absence, and reformed flocs occurred irreversibly, especially with greater irreversibility in the presence of high valent cationic electrolyte. For P-B and P-C forming humic flocs by polyelectrolyte bridging and electrostatic patch effect mechanisms, the breakage of humic flocs did not occur

at high shear rate for the short breakage time applied by the other coagulants. However, at a rather long breakage time (about 15 min), it did not occur for P-B and occurred a little for P-C.

With increasing floc breakage time, the initial floc size decreased more greatly and smaller flocs were reformed for inorganic coagulants, but for P-A, apart from a delay, corresponding to the breakage time, the rate of floc regrowth was about the same in all cases and the FI reached the same value as that before breakage, indicating that the duration of the breakage has no effect on the reformation of the flocs, differently for inorganic coagulants.

Acknowledgements

This work was supported by the research grant of the Cheju National University in 2005.

References

- 1) Rebhun M., Lurie M., 1993, Control of organic matter by coagulation and floc separation, *Water Sci. Technol.*, 27(11), 1-20.
- 2) Tipping E., 1993, Modelling ion binding by humic acids, *Colloids & Surfaces A*, 73, 117-131.
- 3) Smeds A., Franzen R., Kronberg L., 1995, Occurrence of some chlorinated enol lactones and cyclopentane-1,3-diones in chlorine-treated waters, *Environ. Sci. Technol.*, 29(7), 1839-1844.
- 4) Nobukawa T., Sanukida S., 2000, Genotoxicity of halogenated by-products in the disinfected waters, Text of Posters of 1st IWA World Water Congress, Paris, France, Np-049.
- 5) Matsuo T., Unno H., 1981, Forces acting on floc and strength of floc, *J. Environ. Eng. ASCE*, 107, 527-545.
- 6) Brakalov L. B., 1987, A connection between orthokinetic coagulation capture efficiency of aggregates and their maximum size, *Chem. Eng. Sci.*, 42, 2373-2383.
- 7) Mühle K., 1993, Floc stability in laminar and turbulent flow, *In Dobias, B. (Ed.), Coagulation and Flocculation*. Dekker, New York, pp. 355-390.
- 8) Gregory J., Rossi L., 2001, Dynamic testing of water treatment coagulants, *Water Sci. Technol.: Water Supply*, 1(4), 65-72.
- 9) Serra T., Colomer J., Casamitjana X., 1997, Aggregation and breakup of particles in a shear flow, *J. Colloid Interface Sci.*, 187, 466-473.

- 10) Bache D. H., Johnson C., McGilligan J. F., Rasool E., 1997, A conceptual review of floc structure in the sweep floc domain, *Water Sci. Technol.*, 36(4), 49-56.
- 11) Leentvaar J., Rehbun M., 1983, Strength of ferric hydroxide floes, *Water Res.*, 17, 895-902.
- 12) Duan J., Gregory J., 2003, Coagulation by hydrolysing metal salts, *Adv. Colloid Interface Sci.*, 100-102, 475-502.
- 13) Francois R. J., 1987, Strength of aluminium hydroxide floes, *Water Res.*, 21, 1023-1030.
- 14) Spicer P. T., Pratsinis S. E., Raper J., Amal R., Bushell G., Meesters G., 1998, Effect of shear schedule on particle size, density, and structure during flocculation in stirred tanks, *Power Technol.*, 97, 26-34.
- 15) Clark M. M., Flora J. R., 1991, Floc restructuring in varied turbulent mixing, *J. Colloid Interface Sci.*, 147, 407-421.
- 16) Gregory J., Li G., 1991, Effects of dosing and mixing conditions on polymer flocculation of concentrated suspensions, *Chem. Eng. Comm.*, 18, 3-21.
- 17) Ray D. T., Hogg R., 1987, Aggregate breakage in polymer-flocculated suspensions, *J. Colloid Interface Sci.*, 116(1), 256-268.
- 18) Bolto G. A., 1995, Soluble polymers in water purification, *Prog. Polym. Sci.*, 20, 987-1041.
- 19) Xu M. L., Lee M. G., Kam S. K., 2005, Comparison of flocculation characteristics of humic acid by inorganic and organic coagulants: effects of pH and ionic strength, *J. Environ. Sci.*, 14(8), 723-737.
- 20) Lee M. G., Kam S. K., 2005, Charge determination of cationic polyelectrolytes by visual titrimetry and spectrophotometry, *J. Environ. Sci.*, 14(6), 525-532.
- 21) Griebel T., Kulicke W. M., 1992, Molecular characterization of water-soluble cationic polyelectrolytes, *Makromol. Chem.*, 193, 811-821.
- 22) Gregory J., Chung H. J., 1995, Continuous monitoring of floc properties in stirred suspensions, *J. Water Supply: Res. Technol.*, AQUA, 44, 125-131.
- 23) Kam S. K., Kim D. K., Lee M. G., 2003, Effects of polyelectrolyte dosage, kaoline particles and pH on flocculation of humic acid by cationic polyelectrolytes, *J. Environ. Sci.*, 12(8), 861-870.
- 24) Gregory J., 1996, Polymer adsorption and flocculation, In Finch, C. A. (ed.), *Industrial Water Soluble Polymers*, Royal Society of Chemistry, Cambridge, UK, pp. 62-75.
- 25) Yukselen M. A., Gregory J., 2004, The reversibility of floc breakage, *Int. J. Miner. Process*, 73, 251-259.
- 26) Gray S. R., Ritchie C. B., 2006, Effect of organic polyelectrolyte characteristics on floc strength, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 273, 184-188.
- 27) Durand-Piana G., Lafuma F., Audebert R., 1987, Flocculation and adsorption properties of cationic polyelectrolytes toward Na-montmorillonite dilute suspensions, *J. Colloid Interf. Sci.*, 119, 474-480.
- 28) Horn A. F., Merrill E. W., 1984, Midpoint scission of macromolecules in dilute solution in turbulent flow, *Nature*, 312, 140-141.
- 29) Kretzschmar R., Holthoff H., Sticher H., 1998, Influence of pH and humic acid on coagulation kinetics of kaolinite: a dynamic light scattering study, *J. Colloid Interface Sci.*, 202, 95-103.
- 30) Zhou J. L., Rowland S., Mantoura R. F. C., Braven J., 1994, The formation of humic coatings on mineral particles under simulated estuarine conditions- a mechanistic study, *Water Res.*, 28(3), 571-579.
- 31) Yukselen M. A., Gregory J., 2002, Breakage and re-formation of alum floes, *Environ. Eng. Sci.*, 19, 229-236.