Evaluation of mixing conditions using an on-line monitoring technique

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Abstract−Effects of mixing conditions on flocculation were investigated by using a photometric dispersion analyzer (PDA) as an on-line monitoring technique in this study. Both river water and synthetic waters of humic acid (HA) and kaolin solutions were used and polyaluminum chloride (PACl) were used as a coagulant in this study. A clear relationship between F-index and residual turbidity was observed. Residual turbidity was low at high F-index. The mixing effects were also found closely related to the floc formation. When the floc formation was governed by a combination of charge neutralization and sweep floc, rapid mixing was important, but it was not important when the floc formation was governed by the sweep floc mechanism. The coagulant dosage governed the floc size and strength in the sweep floc region. The higher the coagulant dosage was, the larger but the weaker the floc was. Rapid mixing effects were different, depending on raw water characteristics. Fast and large floc formation was observed in flocculation of the kaolin solution, compared to that of the HA solution. Small HA would be mostly adsorbed onto the hydroxide precipitate after the precipitate formed. The adsorption could retard further floc growth. The resulting floc was small, and the floc formation was slow. However, kaolin helped flocculation by bridging the hydroxide precipitates, leading to fast and large floc formation. Temperature affected the flocculation kinetics as well as the floc size. A large floc formed at high temperature. The flocculation kinetics became fast with increasing temperature.

Key words: F-Index, On-line Monitoring, Photometric Dispersion Analyzer (PDA), Rapid Mixing, Flocculation, Temperature

INTRODUCTION

Rapid mixing is the most important process in water treatment because raw water coming into a water treatment plant generally receives the first treatment at a rapid mixing basin. Coagulant is added into raw water in this basin. The coagulant addition then causes particle destabilization and hydroxide precipitation. As reported by Stumm et al. [1], metal coagulant would undergo hydrolysis once being injected and then form metal hydroxide precipitates. Vik et al. [2] added that coagulation would occur through contact and adsorption stages. Coagulation is a quick process. Amirtharajah et al. [3] reported that it took less than 1 second for hydrolysis products to adsorb onto colloids by charge neutralization and 1-7 seconds for sweep coagulation between hydroxide precipitate and colloids. Therefore, the purpose of rapid mixing is to disperse coagulant instantaneously into raw water so that colloidal particles can have uniform contact with the coagulant.

The reaction between colloids and coagulant is affected by raw water characteristics and mixing conditions. These water characteristics include temperature, pH, alkalinity, suspended matter, organic matter, conductivity, etc., while the mixing conditions include intensity and contact time. The mixing intensity has been traditionally represented by the velocity gradient (G) since Camp et al. [4] introduced the concept. Since G is affected by viscosity, water temperature also becomes important for mixing intensity.

It is difficult to interpret and evaluate coagulation results because so many factors are involved in coagulation. The normal practice

in water treatment is a jar test. Operators and researchers often rely on jar tests to determine coagulant dosage and evaluate coagulation efficiency. However, jar test has its limitations. Certain conditions are preset, and only those specified mixing conditions can be evaluated in the test. Unfortunately, the optimum condition does not necessarily coincide with those specified conditions. If the optimum mixing time is less than the specified condition, unnecessary energy consumption results. If the optimum time is greater, then treated water quality can degrade. Therefore, it is necessary to monitor the coagulation process in real time scale. PDA was introduced to do just that. Gregory [5] showed that the root mean square (V_{rms}) value of the light fluctuation is a function of the square root of the V_{rms} of the particle concentration and particle size. By measuring the V_{rms} of a fluctuating signal and the average light intensity (V_{dc}), the aggregation or breakup in a flocculation process can be calculation as Eq. (1).

$$\text{F-index} = \frac{V_{rms}}{V_{dc}} = \sqrt{\frac{NL}{A}}C$$

V_{rms} : fluctuating component
V_{dc} : steady component
N : number concentration of colloid
L : length of optical path
A : effective cross sectional area of light beam
C : cross section of scattered light

Gregory [5,6] and Burgess et al. [7] maintained that flocculation index (F-index) is directly related to floc size. A large F-index value indicates the formation of large floc. Since large floc settles well, a large F-index value would result in low residual turbidity. Kan et

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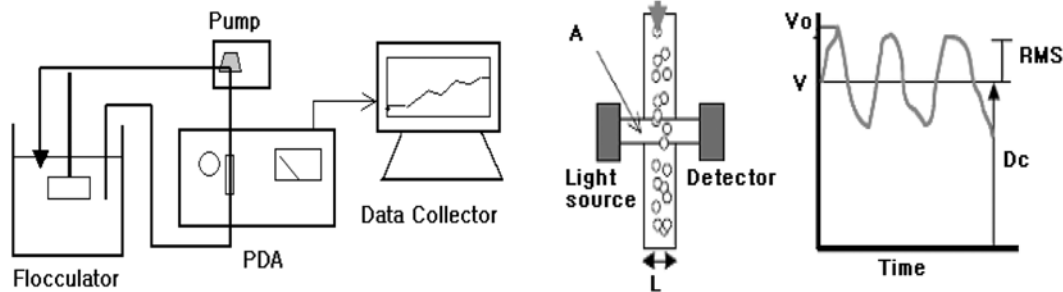E-mail: eeenvlyd@cheju.ac.kr

Fig. 1. PDA setting configuration of measuring floc growth and data result with time.

al. [8] investigated the relationship between F-index and residual turbidity. They found that residual turbidity was low when F-index was large. This study evaluated the effects of mixing conditions on flocculation by using on-line monitoring.

MATERIALS AND METHODS

Both synthetic and natural waters were used in this study. Kaolin (Junsei Chemical), or humic acid (Aldrich Chemical) was added to distilled water to make synthetic waters of the kaolin and the HA solutions. The turbidity of the kaolin solution was 58-80 NTU. The concentration of humic acid in the HA solution was either 1 or 3 mg/L. Alkalinity was added by using the bicarbonate solution, which was prepared by dissolving $NaHCO_3$ in distilled water. The pH of the bicarbonate solution was adjusted to 8.2 by sulfuric acid before use. Nakdong river, which is major drinking water source for southeastern Korea, was used as a natural water source.

The schematic flow of the PDA experiment is illustrated in Fig. 1. Flocculated water in the jar was fed continuously into the PDA during flocculation time through the tube and the F-index of flocculated water was measured. While particles pass the lighted area, light fluctuations are generated from random variations of the suspended particle size. The detected light intensity was transferred to voltage. V_{dc} is the average transferred light intensity and V_{rms} is the root mean square value.

A jar test was used for experiments with a peddle-type impeller (76 mm×25 mm). Two coagulants were used: PACl and liquid alum. PACl has an aluminum (Al) content of 5.3% as Al and liquid alum with Al content of 4.2%. Undiluted coagulant was added to the surface of the waters with a micropipette. When necessary, the coagulated water was transferred to a filter column for a filtration test.

The size of the filter, which was set beside the jar-tester, was 3.0 cm×3.0 cm with 12 cm in depth. The effective size of the filter media was 0.92 mm. During the filtration test, flocculated water was continuously fed into the filter from the flocculation reactor during flocculation through a pump and the filtrate was collected to measure residual turbidity.

A specially manufactured jar with double jacket made of stainless steel was used to evaluate the temperature effect. After the water temperature of the cooler was adjusted to the predetermined value, it was transferred to the jacket. Then, the desired water temperature was reached through water circulation in the jacket. Turbidity of raw, settled, filtered waters was measured with a turbidimeter (HACH 2100AN). The particle distribution was measured by using the particle size systems (model 770, Accusizer). On-line monitoring of flocculation was conducted with iPDA (Econovel company).

RESULTS AND DISCUSSIONS

1. Relationship between F-Index and Residual Turbidity

In order to examine the relationship between F-index and residual turbidity, liquid alum was added at 30 mg/L and 50 mg/L to the natural water. Rapid mixing was given for 5 seconds at 180 rpm. Flocculation was monitored while slow mixing was given at 40 mg/L. Fig. 2 shows the change in F-index values with flocculation time together with settled and filtered turbidities. The F-index value increased immediately after the alum addition. The linear increase continued for about 250-300 seconds, and then fluctuated between 0.1 and 0.4. According to Hopkins et al. [9], this period corresponds to the time in which both floc formation and breakage occurred.
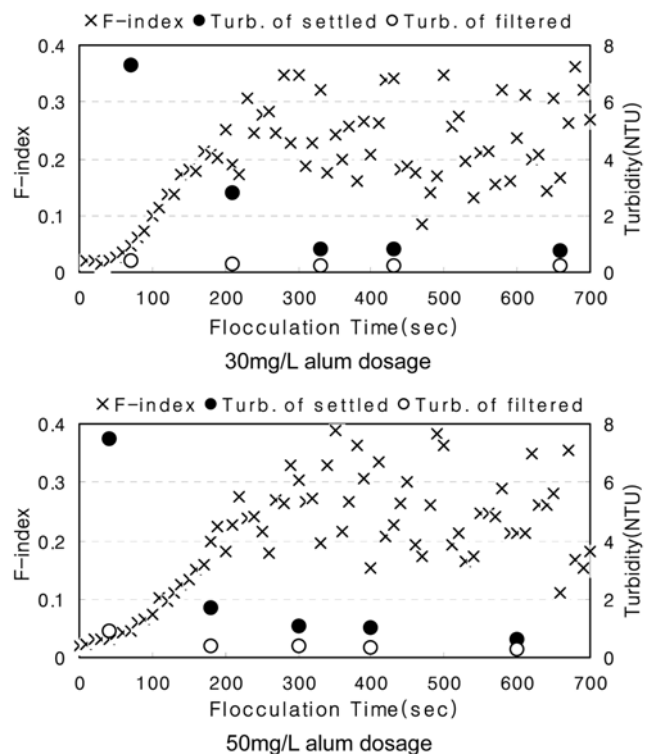
Fig. 2. Comparison of F-index and residual turbidity of settled and filtered water at 30 and 50 mg/L of alum.

Comparison of F-index values with the corresponding residual turbidities indicated that there was clearly a relationship between them. When F-index values were low at the beginning of flocculation (40 seconds), their settled turbidities (7.3, 7.5 NTU) were high, close to the initial value (9 NTU). After about 3 minutes of flocculation, F-index value increased, and accordingly, the settled turbidities decreased (2.8, 1.7 NTU). Further flocculation (5 minutes) ended the linear increase. Although F-index values fluctuated since then, the settled turbidities remained unchanged. This result confirms a strong relationship between the F-index and settled turbidities, as indicated by Kan et al. [8], which enables the evaluation of flocculation performance using the F-index. Since the validity of the F-index was verified, flocculation was evaluated by using the F-index in the following experiments. The filtered turbidity results showed a different pattern. At the beginning of increasing the F-index before 60 seconds flocculation time, the flocs were formed to filter easily, showing low filtered turbidity. This means that these flocs were in filterable sizes. Although they could not be separated by sedimentation, they were large enough for filtration.

3. Effects of Rapid Mixing Conditions on Flocculation

In order to evaluate the effects of rapid mixing conditions on flocculation, PACl was added to the natural water at a dosage of 30 ppm. The mixing intensities were fixed at 180 and 340 rpm, while various rapid mixing times (5, 10, 20, 40, 60 seconds) were given. After rapid mixing, floc formation was monitored while slow mixing was done at 40 rpm. Fig. 3(a) shows the results at a lower intensity (180 rpm), as well as at a higher intensity (340 rpm). Examination of this figure reveals that the linear increase in F-index values stopped in about 200-400 seconds. Then, it fluctuated, indicating both floc breakage and formation. Comparison of F-index values during this fluctuating period showed that the lower intensity (180 rpm) produced flocs with larger F-index values than the higher intensity (340 rpm). This means that the lower the intensity was, the larger the floc was. Rapid mixing time also affected the floc size. F-index values became

larger with short rapid mixing time. These results indicate that low intensity and short mixing time would be beneficial for a large floc. Rapid mixing should be provided for a short period of time at lower intensity if formation of large floc is desired.

Then, experiments were repeated at higher dosage (40 mg/L) with three intensities of 180, 280, and 380 rpm. Fig. 3(b) shows the results. According to Fig. 3(b), F-index values were higher at 40 mg/L than 30 mg/L. The difference was more evident at the low mixing intensity. Similar results were obtained as with 30 mg/L. The lowest intensity produced flocs with the largest F-index values. The increase in the mixing intensity resulted in a decrease in F-index values. However, there was no big difference in F-index values between 280 rpm and 380 rpm. The effect of mixing time was also observed. F-index values decreased with increased mixing time. The effect became evident at the high intensity and broken flocs during long rapid mixing time were not easily reformatted.

4. Effects of Rapid Mixing Conditions on Residual Turbidity

In order to evaluate the effects of rapid mixing conditions on residual turbidity, various dosages of PACl (10, 20, 30, 40 mg/L) were added to the natural water with initial turbidity of 9 NTU. The rapid mixing intensities were fixed at 180 and 340 rpm, while the mixing time was varied to 0, 5, 10, 20, 40, 60 seconds. Slow mixing was given at 40 rpm for 9 minutes. Supernatant was taken to measure residual turbidity after 20 minutes of sedimentation. Fig. 4 shows the results. When enough coagulant was added to promote formation of sweep floc (20-40 mg/L), residual turbidities at 20, 30mg/L dosage were low regardless of mixing conditions.

Effects of mixing conditions were different, depending upon the coagulant dosage. High mixing intensity resulted in low residual turbidities at the 10-30 mg/L and in high residual turbidities at the 40 mg/L. These results are in line with the F-index results. F-index values decreased with increasing rapid mixing time. The decrease was more evident at high mixing intensity. However, such effect was not evident at the low dosage. When intense rapid mixing (340
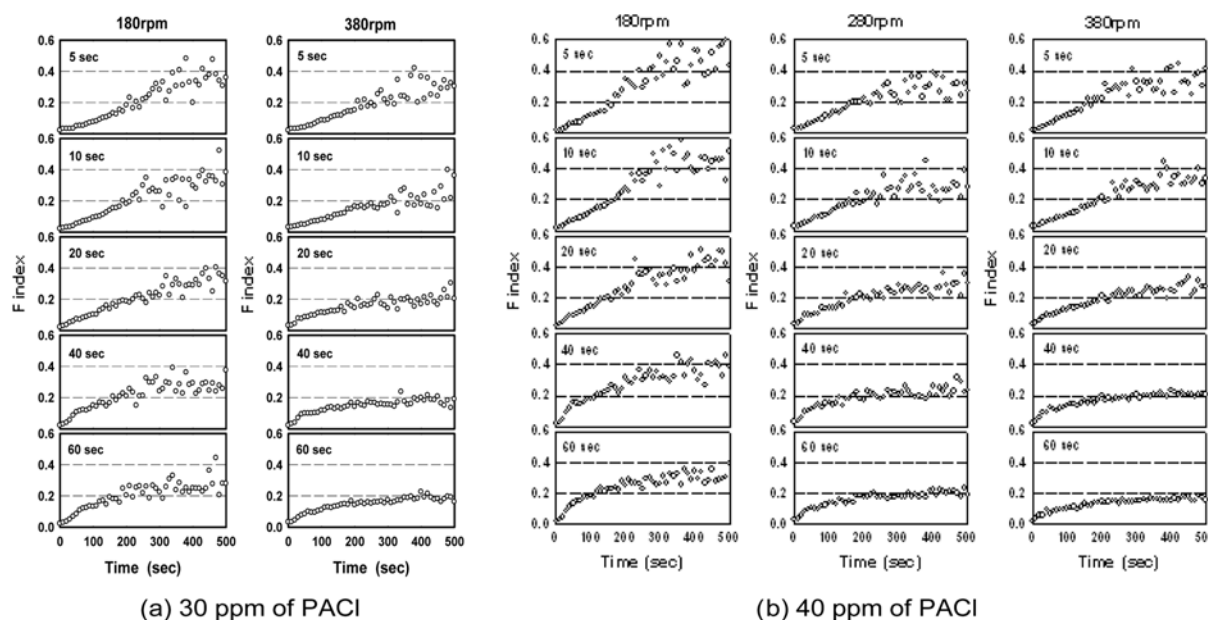

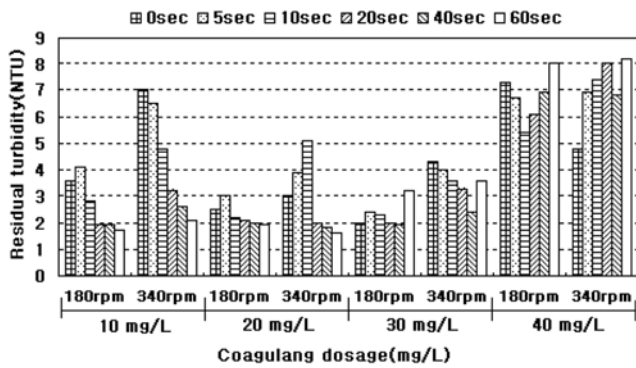Fig. 3. F-index monitoring at different conditions of rapid mixing at 30 and 40 mg/L of PACl.

Fig. 4. Residual turbidity at different conditions of rapid mixing at 10, 20, 30, 40 mg/L of PACl (The values on legend are rapid mixing time).

rpm) was extended for a long period (60 seconds) at 10 mg/L, the lowest residual turbidity was obtained. Effects of mixing time were different even at the high dosages. All of the residual turbidities were similar at the dosage of 20 mg/L after 5 seconds of rapid mixing at 180 rpm. This indicates that mixing time was not important at this dosage, provided that the minimum amount of rapid mixing (5 seconds at 180 rpm) was given. This result does not necessarily mean that rapid mixing should be omitted. When rapid mixing was absent, residual turbidities were high. Completely different results were observed at the higher dosages (30 and 40 mg/L). The lowest residual turbidity was obtained without rapid mixing. Residual turbidity increased with mixing time. The increase was more evident at the higher PACl dosage (40 mg/L). The increase was also observed even at 20 mg/L when the mixing intensity was high (340 rpm). The higher the intensity, and the longer the mixing time was, the higher the residual turbidities were. According to literature [10,11], the optimal coagulation could be determined with stream current detector (SCD) but good flocculation condition depended on not only the optimal coagulant but also mixing intensity.

5. Floc Characteristics

The above results suggest that floc characteristics were different, depending on coagulant dosage. According to the coagulation diagram [3], PACl dosages of 20-40 mg/L and that of 10 mg/L belong to different regions. The high dosages belong to the sweep floc region, and the low dosage to the combination region. Sweep floc enmeshment is responsible for coagulation in the sweep floc region, while both charge neutralization and sweep floc enmeshment are responsible for coagulation in the combination region. Since coagulation was governed by different mechanisms, effects of rapid mixing were different. Rapid mixing was important at the low dosage, but not at the high dosages. Rapid mixing was important at the low dosage at which colloids were coagulated by charge neutralization because it was essential to promote contacts between coagulant and colloids. Therefore, the lowest residual turbidity was obtained under the most intense mixing condition (60 seconds at 340 rpm).

Rapid mixing at the high dosages was not as important as at the low dosage. The flocs formed at the same sweep floc region had different characteristics, depending on coagulant dosage. The flocs formed at the low dosage (20 mg/L) were smaller, but stronger. On the other hand, those formed at the high dosages (30, 40 mg/L) were larger, but weaker. It seems that the dosage of 20 mg/L was insuffi-

cient to promote rapid formation of large hydroxide precipitate. Although the precipitates did form, they did not settle well without rapid mixing because they were small. However, slight rapid mixing helped because it could promote the precipitate formation. The floc was strong enough to sustain the mild intensity (180 rpm), but not enough for the high intensity (340 rpm). The high intensity broke the floc, resulting in high residual turbidities. The dosages of 30 and 40 mg/L were sufficient enough to promote rapid formation of large hydroxide precipitate. The large flocs formed instantaneously at these dosages. This resulted in low residual turbidities even without rapid mixing. Although large, it was weak. The floc breakage occurred even at the mild intensity (180 rpm). More mixing led to more breakage. The higher the dosage was, the weaker the floc was.

6. Effects of Raw Water on Flocculation

In order to examine effects of raw water on flocculation, PACl was added to the kaolin solution as well as to the HA solution at various dosages. Rapid mixing was given for 10 seconds at 180 rpm. A change in F-index values was monitored with time while slow mixing was given at 40 rpm. Fig. 5(a) shows the results for the kaolin solution. The F-index started to increase about 40 seconds after the PACl addition. It linearly increased until it reached the fluctuating period at about 250-300 seconds. As observed above, high dosage resulted in a large floc. The higher the PACl dosage was, the larger the F-index value was. Since F-index values were similar after PACl dosage was greater than 50 mg/L, the optimum dosage could be 50 mg/L. This suggests that the optimum dosage could be found by using the F-index. Fig. 5(b) shows the results for the HA solution. Comparison of the flocculation results of the kaolin solution with those of the HA solution reveals that floc formed faster in the kaolin solution than in the HA solution. The F-index started to increase about 150 seconds after the PACl addition (30 mg/L) in the HA solution. Higher dosage expedited the floc formation by 50 sec-
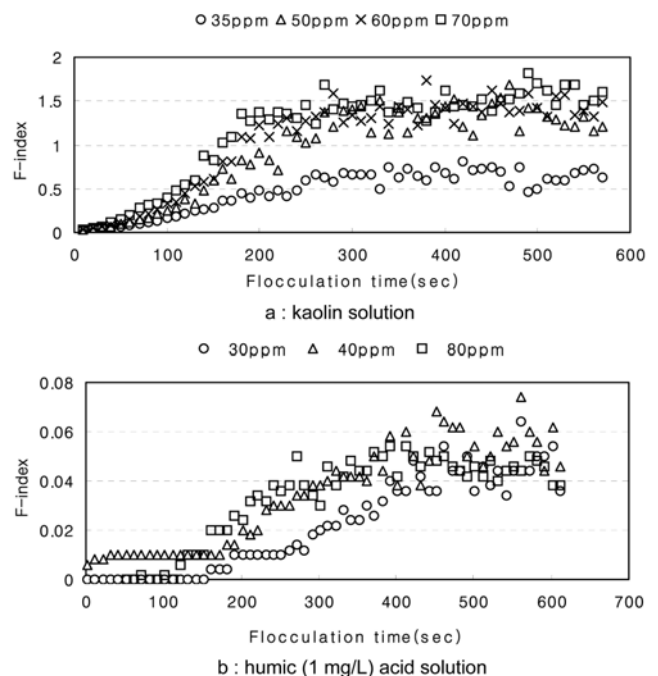

Fig. 5. F-Index monitoring results by PACl dosages for kaolin and humic acid solution.
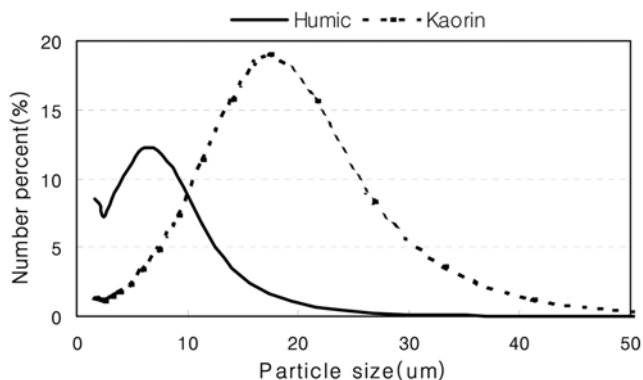
Fig. 6. Comparison of particle size distributions of the kaolin and the HA solutions.

onds, which was still slower than 40 seconds. It also took more time for floc growth due to the late start in the HA solution. The F-index reached the fluctuating period at about 400 seconds.

Another difference was the magnitude of F-index values. F-index values were substantially higher for the flocs formed during flocculation of the kaolin solution than those formed during flocculation of the HA solution. This result indicates that floc size depended on raw water characteristics. Flocculation of the kaolin solution resulted in larger flocs than that of the HA solution. This could be explained by different floc formations in the kaolin and the HA solution. Fig. 6 shows the size distribution of the HA and kaolin solutions. According to Fig. 6, HA is substantially smaller than a kaolin particle. Small HA would mostly adsorb onto the hydroxide precipitates after the precipitates form. The adsorption could, then, retard the floc growth. Therefore, the floc growth was slow, and the resulting floc was small in flocculation of the HA solution. On the other hand, kaolin, which was mostly larger than the initial hydroxide precipitate, could participate in flocculation by accumulation of the precipitates. Although not shown here, the flocculation results were similar to those of the kaolin solution when both kaolin and HA were added together to make the synthetic water. This result indicates that different mixing time should be provided depending on raw water characteristics. Longer mixing time would be beneficial for flocculation of the HA solution.

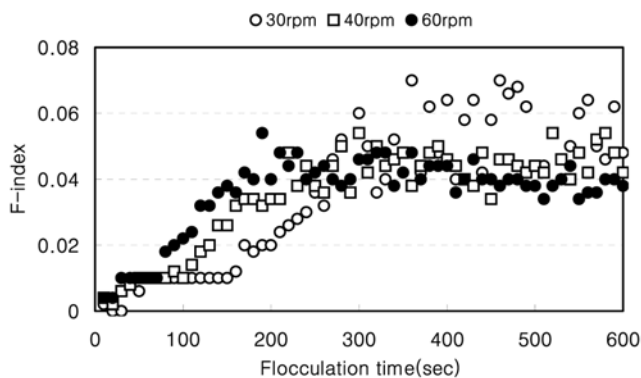## 7. Effects of Slow Mixing Conditions on Flocculation

Fig. 7. F-Index monitoring at different slow mixing intensities (3 mg/L of HA solution).

a: normal temperature
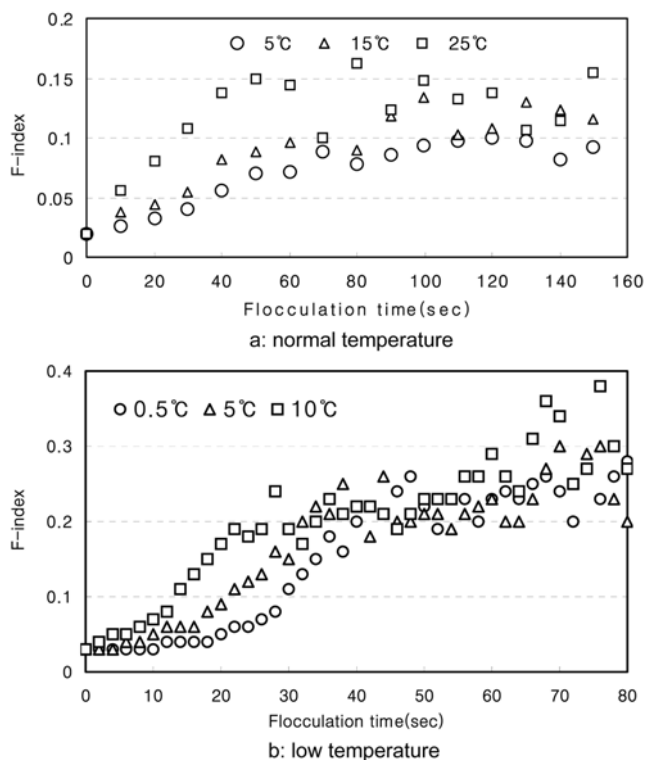

b: low temperature

Fig. 8. F-Index monitoring at various temperatures.

In order to examine slow mixing intensity on flocculation, PACl was added to the HA solution (3 mg/L) at 70 mg/L. Rapid mixing was given for 10 seconds at 180 rpm. A change in F-index values was monitored while three different intensities of slow mixing were given. Fig. 8 shows the results. According to Fig. 7, the flocculation kinetics depended on the mixing intensity of slow mixing. High intensity expedited the floc formation. F-index started to increase in about 70 seconds at 60 rpm, while the increase was not observed until about 160 seconds at 30 rpm. However, the higher intensity resulted in low values of F-index. This result means that higher intensity of slow mixing would expedite the floc formation, but produce smaller flocs.

8. Effects of Temperature on Flocculation

In order to examine temperature effects, flocculation was performed at 5-25 °C. Fig. 8(a) shows the results. As expected, the higher the temperature was, the faster the floc formation or the increase in F-index value was. The flocculation kinetics was, then, calculated using F-index values, as shown in Eq. (2). Table 1 summarizes the calculation results. According to Table 1, the temperature increase from 5 °C to 25 °C expedited the floc formation by 2.6 times. It is interesting to note that the F-index values were high at high temperature. According to Table 1 and Fig. 8(a), F-index values increased

Table 1. Flocculation kinetics in accordance with temperature

Temperature	5 °C	10 °C	15 °C	20 °C	25 °C
$F\text{-index}_0$	0.02	0.02	0.02	0.02	0.02
$F\text{-index}_{50}$	0.07	0.08	0.09	0.12	0.15
Rv, $second^{-1}$	0.0010	0.0012	0.0014	0.0020	0.0026

with temperature, which indicates that temperature also affects the floc size. High temperature resulted in a large floc at the faster rate. According to Fitzpatrick et al. [12], high temperature induced rapid flocculation. The flocculation results at low temperatures (<10 °C) are shown in Fig. 8(b). This figure clearly shows that the floc formation became slow as the temperature decreased. Therefore, the coagulant dosage or/and the rapid mixing intensity should be increased in order to expedite the floc formation at low temperatures.

$$Rv, second^{-1} = (F\text{-}index_{50} - F\text{-}index_0)/50 \qquad (2)$$

CONCLUSIONS

Effects of mixing conditions on flocculation were investigated by using an on-line monitoring technique in this study. A clear relationship between F-index and residual turbidity was observed. Residual turbidity was low at high F-index. Therefore, the F-index could be a helpful parameter for operators at a water treatment plant. They can manage the flocculation process simply by monitoring on-line F-index values. When the floc formation was governed by a combination of charge neutralization and sweep floc, rapid mixing was important. However, rapid mixing was not important when the floc formation was governed by the sweep floc mechanism. Rapid mixing was unnecessary in this region because coagulant dosage was sufficient enough to promote the rapid formation of large hydroxide floc. Rapid mixing was rather detrimental by causing floc breakage. The floc formed in this region was large, but weak. Subsequently, rapid mixing easily broke the floc. The coagulant dosage governed the floc size and strength. The higher the coagulant dosage was, the larger, but weaker, the floc was. It is, therefore, important to provide proper rapid mixing conditions in water treatment, depending on the floc formation and coagulant dosage. When the coagulant dosage belongs to the combination region, intense rapid mixing should be provided so that a large floc would form rapidly. When the coagulant dosage belongs to the sweep floc region, it would be more beneficial to omit rapid mixing so that floc breakage could be avoided.

Rapid mixing effects were different, depending on raw water characteristics. Although the same mixing conditions were provided, floc formed substantially faster during flocculation of the kaolin solution than that of the HA solution. The floc formed in the kaolin solution was also larger than the one formed in the HA solution. The different floc formation could cause the difference. Small HA would be mostly adsorbed onto the hydroxide precipitates after the

precipitate formed. The adsorption could retard further floc growth. The resulting floc was small, and the floc formation was slow. However, kaolin helped flocculation by bridging the hydroxide precipitates, leading to the large and fast floc formation. Temperature affected the flocculation kinetics as well as the floc size. A large floc formed at high temperature. The flocculation kinetics became fast with increasing temperature. The coagulant dosage or/and the rapid mixing intensity need to be increased in order to expedite the floc formation at low temperature.

REFERENCES

1. W. Stumm and C. R. O'melia, *J. AWWA*, **60**, 514 (1968).
2. E. A. Vik and B. Eikebrokk, *Coagulation process for removal of humic substances from drink water in a aquatic substance: Influence of Fate and treatment of pollutions*, I. H. Suffet and P. A. MacCarthy Eds., 385-408, Symposium by the American Chemical Society, Washington, D.C.
3. A. Amirtharajah and K. M. Mills, *J. AWWA*, **74**, 210 (1982).
4. T. R. Camp and P. C. Stein, *J. Boston Soc. Civil Eng.*, **30**, 219 (1943).
5. J. Gregory, *J. Colloid Interface Sci.*, **105**, 357 (1985).
6. J. Gregory, *Colloids and Surfaces*, **18**, 175 (1986).
7. M. S. Burgess, J. E. Curely, N. Wiseman and T. Kamei, *J. Pulp Pap. Sci.*, **28**, 63 (2002).
8. C. Kan, C. Huang and J. R. Pan, *Colloids and Surfaces A; Physicochemical and Engineering Aspect*, **203**, 1 (2002).
9. D. C. Hopkins and J. J. Ducoste, *J. Colloid Interface Science*, **264**, 184 (2003).
10. J. Wang, *J. AWWA*, **93**, 54 (2001).
11. D. S. Briley, Knappe and R. U. Detlef, *J. AWWA*, **94**, 80 (2002).
12. C. S. B. Fitzpatrick, E. Fradin and J. Gregory, *Water Science and Technology*, (12), 171 (2004).
13. J. Gregory, *Chem. Eng. Sci.*, **36**, 1789 (1981).
14. J. Gregory and H. Chung, *J. Water SRT-Aqua*, **44**, 125 (1995).
15. W. R. Hutchinson and P. D. Foley, *J. AWWA*, **66**, 79 (1974).
16. W. R. Hutchinson, *J. AWWA*, **68**, 79 (1976).
17. H. J. Jung, J. W. Lee and D. Y. Choi, *Korean J. Chem. Eng.*, **23**, 271 (2006).
18. D. J. Kim and K. S. Kim, *Korean J. Chem. Eng.*, **19**, 495 (2002).
19. J. P. Kim, I. S. Han and C. B. Chung, *Korean J. Chem. Eng.*, **20**, 580 (2003).
20. G. E. Sweeny and P. M. Prendiville, *J. AWWA*, **66**, 65 (1974).