USE OF THE FIBER-OPTICAL MONITOR IN EVALUATING THE STATE OF FLOCCULATION

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Abstract—On-line monitoring the state of coagulation/flocculation enables automatic control of coagulation process concerning the condition of the chemical additive. In this study, a new optical monitoring technique is employed to evaluate the extent of flocculation, which involves measuring the fluctuating light intensity transmitted through a flowing suspension. This technique functions as a sensitive monitor providing an empirical index related to the state of aggregation, and could form the basis of an on-line technique. The assessment for feasible application in monitoring the flocculation through this technique is the primary objective of this study. Also, a series of batch flocculation tests is performed under different conditions. These results indicate that the fiber-optical technique is useful in monitoring the state of aggregation with different coagulants and the variation of turbidity conditions. Furthermore, a reliable index related to the floc size is provided and can be applied in determining the optimal dosage of coagulant.

Key words—coagulation, flocculation, optical monitor, floc size, alum, polymer

INTRODUCTION

The coagulant dose in water treatment plants in Taiwan is determined on the basis of the historical data collected by the operators or the trial-and-error data of periodic jar tests. However, excess development in the proximity of water sources has subsequently resulted in high concentration of suspended solid in the river, lake, and reservoirs. The water turbidities may vary from 10 NTU to thousands of NTU in a few hours when heavy rainfall occurs within the area of an upstream watershed. The influent turbidities and subsequently the coagulant demand are time-variant. Therefore, recent attempts to determine the chemical dosage in the coagulation process has frequently failed to adapt to the turbidity variation in the effluent of water treatment plant, such as delayed judgment or inattention during off-duty hours at night. Such an occurrence would result in inefficient settling as well as shortening the filtration run. The dosage determined by these leads to both poor, in real-time, dose control for the highly changeable quality of raw water and the inefficient use of expensive chemicals without an actual dose.

Several methods available to determine the coagulation dose are based on either turbidity measurements or particle counting. Turbidity measurements are relatively easy to take but fail in characterizing the size of floc as well as the state of aggregation. Particle counting is effective only for the highly diluted suspension in order to avoid a coincidental effect and fail to provide real-time responses during the operation. Therefore, an on-line method is required for controlling the chemical dose in the coagulation/flocculation.

A simple but sensitive optical technique has been developed to monitor the state of aggregation of coagulation/flocculation (Gregory, 1985, 1986), which is based on the measurement of fluctuations in the intensity of light transmitted through a flowing suspension. The fluctuations arising from random variations with the mean number of particles in the sample that follow the Poisson distribution, and the root mean square (rms) value of the intensity fluctuations are dependent on the scattering coefficient and the square root of the concentration. By measuring the rms value of the fluctuation signal \( V_{\text{rms}} \) and the average transmitted light intensity \( (d_c) \), the aggregation or deaggregation in the suspension can be quantified regarding the ratio of \( V_{\text{rms}} \) to \( d_c \) (ratio). This ratio value is also represented as flocculation index (F-index) in this study.

The fiber-optical technique has been first introduced by Gregory and Nelson (1984). In their investigation, a comparison has been made of the measured rms of kaolin suspension with varying coagulant dosing. However, the effect of particle concentration and coagulant dose for those different coagulants has not been discussed here. Jackson and Tomlinson (1986) successfully applied this technique in automatic coagulation control. Some other approaches involve characterizing the condition on
alum sludge dewatering (Kayode and Gregory, 1988), evaluating floc size with on-line mode (Matsui and Tambo, 1991) as well as describing dynamics and mechanisms of coagulation (Ching et al., 1994).

The specific objective of this work is to evaluate and refine this optical monitoring technique whilst considering the turbidity variation. Three types of coagulant have been applied here to evaluate its feasibility for widespread application. By changing the coagulant’s dosage, different ratio outputs (F-index) corresponding to various flocculation/settling states have been investigated for the development of in-site operation information.

**MATERIALS AND METHODS**

**Synthetic suspension**

A given amount of kaolin in powder form (Nacalai Tesque) was mixed with tap water (ionic strength = $3 \times 10^{-3}$ N) to prepare a test suspension with desired turbidity. The 20, 80, and 200 NTU turbidity of test suspensions were prepared to simulate the low, middle, and high turbidity conditions in raw water. The size distribution of the kaolin suspension was measured by Coulter Counter (Chennelyzer 256, USA) with a 20-$\mu$m aperture tube (effective range = 0.4–12 $\mu$m). Particles in the suspension had a mean volume diameter of 2.1 $\mu$m with a relatively wide size distribution.

**Preparation of coagulant solution**

The chemicals used as coagulants in this study include aluminum sulfate (Alum, Merck), polyaluminum chloride (PAC), and cationic polymer (Dimethyl Diallyl Ammonium Chloride “Catfloc”, Calgon). Stock solutions of alum with various concentrations were prepared according to the experimental need of dosage. The test solutions of PACI and polymer were prepared by diluting the liquid chemicals to a desired concentration just prior to the addition into the test suspension.

**Experimental setup**

An optical analyzer, photometric dispersion analyser (PDA, Rank Bros., Cambridge, UK), was used to monitor the state of coagulation/flocculation of suspension. A schematic diagram of the experimental apparatus is shown in Fig. 1. The mixing device was an acrylic vessel (PDA, Rank Bros., Cambridge, UK), was used to monitor the mixing vessel to the flow-through detector of PDA, where the ratios of the fluctuations in transmitted light intensity to the average transmitted light intensity were monitored continuously. After flowing through the detector, the suspension in the vessel was agitated by an 80- x 13-mm (15cm x 12cm) with four bafflers. A 11 volume of distilled water through the PDA. The suspension without coagulant addition was then flowed through the detector and the rms output was adjusted to around 0.5 volts.

The pH value was maintained at around 7 while adding a strong base (0.1 M NaOH) or acid (0.1 M NaClO$_4$) in the suspension throughout the experiment. The agitation of mixing vessel was maintained at 300 rpm ($G = 900 \text{s}^{-1}$) in order to provide well contacts for chemicals and particles. Considering the time for mixing, flowing, and stability of PDA reading, the ratio reading was determined at 5 minutes after coagulant was added into the mixing vessel. The major function in the mixing vessel is to complete the contact of chemical with particles. However, a duration of around 4 minutes may cause a slight flocculation in the mixing vessel. Thereafter, the coagulated particles in the mixing vessel were flowed through the coiled tube. In the tube, the particles were aggregated as a result of the shear force of laminar flow in the coiled tube. Flow rate in the conveying tube was 2.5 ml/min, and the Gt value in the tube was calculated to be about 10$^6$ based on the formula derived from Gregory (1987). This particle aggregation can be indicated by a marked increase in the rms value, therefore, also the ratio value of PDA. The coagulated particles in the mixing vessel were then taken to measure their zeta potential with zeta meter (Zeter-Meter System 3.0, Zeter-Meter Inc., U.S.A.).

After recording the ratio value, the suspension in the mixing vessel was taken to run the jar tests (Jar Tester, Phips & Bird, USA) for slow mixing (17–20 rpm, 20 min) and quiescent settling (20 min). Consequently, zeta potential (as measured previously), residual turbidity (turbidimeter, HACH, USA) and ratio output of PDA (represented as F-index) corresponding to various dosages of alum were obtained. The same procedure was repeated for the testing of PACI and polymer (Catfloc).

**RESULTS AND DISCUSSION**

**Optimal dosage of coagulants**

(1) Aluminum sulfate. The change of F-index with the alum dosage for the 20 NTU turbidity of kaolin suspension is shown in Fig. 2. The residual turbidity of these suspensions, measured after mixing and settling, is included in this figure. With the increase
of dosage, the F-index is increased from the initial value of 0.5 up to a maximum value of 2.5, and then declines to a stable value of 1. The maximum of the F-index corresponds to the lowest value of the residual turbidity, thereby verifying the effectiveness of the F-index for the determination of optimal coagulant's dosage. The results for the suspension with either 80 or 200 NTU turbidity also exhibit a similar relationship between the F-index and the residual turbidity (data is not shown). Notably, the raise of residual turbidity of water is insignificant when the alum is dosed beyond the optimal condition. Dentel (1991) has pointed out that the mechanism of alum coagulation at neutral pH is the charge neutralization and enmeshment or the enmeshment in major. Although the overdose of coagulant may result in the re-stabilization of particles, the floc formed by those particles is still large and sufficiently dense to settle in the jar tests.

Figure 2 also shows the F-index of flocculated particles corresponding to the zeta potential of coagulated particles. This figure reveals that, in spite of initial turbidity, the coagulated particles possessing isoelectric point of zeta potential on the surface produce the maximum ratio value (F-index). This occurrence indicates that when the alum coagulation reaches the optimal state, at which the surface charge of kaolin may be neutralized, the optimal floc is then formed. Beyond the optimal state, the reversal of the surface charge of coagulated particles occurs as too much alum interacts with kaolin, in which the F-index of flocculated particles decreases with an increase in the coagulant dosage. We can expect that the peak or plateau of the ratio curve may offer a reliable index to determine the optimal dosage of alum.

(2) PACI. The trend of F-index curves for PACI is theoretically similar to those for alum as shown in Fig. 3. According to the zeta potential of coagulated particles, the coagulated particles possess the net positive charge as the F-index reaches a maximum value. Dentel (1991) points out that the colloidal PACI particles possess a relatively high area-to-volume ratio, thereby resulting in the effective adsorption onto the negatively charged particles through the charge neutralization. Therefore, the surfaces of particles coated with PACI still offer some sites which are available for the adsorption of polynuclear alum complex. This results in the continuous growth of aggregated particles until the saturation of adsorption. Furthermore, the coagulated particles bring the positive charge as the growth of floc reaches the maximum state.

The required dosage for PACI in the coagulation/flocculation process is only about half of that for...
alum according to the results from real-plant study of Kaeding et al. (1992). However, our results indicate that the dosage of PACI with respect to the maximum value of the F-index is higher than alum. In the case of 20 NTU, 1.4 mg/l as Al of alum is required to reach a maximum of F-index (Fig. 2). However, 7.3 mg/l as Al of PACI is required to obtain an optimum state of flocculation (Fig. 3). Due to the better flocc formation of PACI than alum, the required dosage of PACI to form the floc, i.e., sufficiently large to settle, is much less than the dosage required for the formation of the largest floc. This fact infers that the F-index of PACI coagulation with the optimal dosage corresponding to the effective settling is less than the maximum value of the F-index curve as shown in the figure. Therefore, it is expected that the control strategy for PDA by measuring the F-index for alum is different from that for PACI. However, the ratio value of PDA is undoubtedly an effective index to evaluate the state of either alum or PACI coagulation.

(3) Polymer. The changes of F-index with the dosage of polymer for the 20 NTU, 80 NTU and 200 NTU turbidity of kaolin suspensions have been investigated with the same procedure as alum. The typical result for 20 NTU turbidity of suspension is shown in Fig. 4. The curve for the F-index corresponding to the polymer dosage exhibits a sharper peak than those to the alum dosage. According to the residual turbidity of supernatant after jar-mixing/settling, the maximum of the F-index corresponds to the lowest of residual turbidity. Once the polymer dosage is over the saturation of polymer bridging, surplus polymer has a tendency to destroy the polymer bridging between particles. This would consequently result in the decrease of floc size as well as the increase of residual turbidity after settlement.

Zeta potential results indicate that the particles are coagulated by a certain amount of polymer to form the largest floc, on which the surface still brings a slight negative charge. More negative charges occur on this so called “largest floc” as original particle concentration (initial turbidity) of suspension is increased. This phenomenon can be accounted schematically as Fig. 5. For dilute suspensions, the particles are coated by the polymer with an optimal dosage to neutralize their surface charges, thereby resulting in zero electrophoretic mobility of the coagulated particle. As Gregory (1987b) has indicated, for cationic polymer and negative particles, charge neutralization plays a large part in the flocculation process. However, in the case of high particle concentration (that is 200 NTU of turbidity in this study), an optimal dosage of polymer to form the largest floc is unnecessary to neutralize surface charges of original particles. Unlike alum and PACI, the raise of residual turbidity of supernatant after sedimentation is observed to be significant when the polymer is overdosed in the suspensions. This phenomenon occurs since the coagulation mechanisms for polymer are adsorption and bridging rather than surface precipitation for aluminum salt. The changes of F-index with the dosage of polymer for the 20 NTU turbidity of kaolin suspensions have been investigated with the same procedure as alum. The typical result for 20 NTU turbidity of suspension is shown in Fig. 4. The curve for the F-index corresponding to the polymer dosage exhibits a sharper peak than those to the alum dosage. According to the residual turbidity of supernatant after jar-mixing/settling, the maximum of the F-index corresponds to the lowest of residual turbidity. Once the polymer dosage is over the saturation of polymer bridging, surplus polymer has a tendency to destroy the polymer bridging between particles. This would consequently result in the decrease of floc size as well as the increase of residual turbidity after settlement.

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overdose of polymer produces restabilized particles since no sites are available for the formation of bridge, thereby resulting in the rupture of floc by extending mixing (Weber, 1972).

Coagulant effect

Table 1 summarizes the maximum of the F-index with three different coagulants; alum, PACI, and polymer at three different turbid conditions. The residual turbidity of supernatants corresponding to each optimal dosing of coagulants after jar-mixing/settling are also included. The PACI clearly has the largest value of maximum at each turbid condition among the three coagulants. This result infers that the flocs produced by PACI are larger than the other two coagulants. This phenomenon results from the polynuclear aluminum complexation of PACI during flocculation, ultimately enhancing particle aggregation, floc formation and settling. The measurements of residual turbidity in the supernatant after jar-mixing/settling also provide this evidence, for which the value of residual turbidity corresponding to the maximum of the F-index for PACI coagulation is lower than the residual turbidity while using alum or polymer as a coagulant. This table also indicates that F-index value for the polymer coagulation is lower than alum coagulation only under the 20-NTU condition. However, the values are higher than alum coagulation under 80 and 200-NTU conditions. The optimal conditions for the alum and polymer coagulation with middling turbid water produce the similar size of floc. The size of the largest floc formed by polymer coagulation with highly turbid water is significantly larger than that formed by alum coagulation, and conversely that size is smaller than that formed by alum coagulation for the low turbidity (20 NTU) condition. Gregory (1987b) has indicated that the flocs produced by polymers are considerably stronger and larger than aggregates formed by alum coagulation. Under the low turbidity condition, there are insufficient particles to provide adequate collision among particles, thereby resulting in excess segment of polymer folding back onto the particle surface. Therefore, this insignificant action of polymer bridging produces small floc during the flocculation.

CONCLUSION

The output value of PDA can accurately reflect the state of initial formation of floc. The maximum of this ratio value related to the best formation of floc is a reliable index for the determination of the optimal dosage for alum and polymer coagulation. The ratio value of PACI coagulation with the optimal dosage corresponding to the effective settling is less than the maximum of ratio value. Results obtained in this study indicate that this fiber-optical technique is a feasible tool in monitoring the flocculation behavior as well as in determining the dosage of alum, PACI and polymer for the varying turbid water.

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REFERENCES