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DUAL WAVELENGTH PHOTOMETRIC DISPERSION ANALYSIS OF COAGULATION AND FLOCCULATION

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ABSTRACT

A technique to evaluate the coagulation/flocculation process on fluctuating light intensity transmitted through a flowing suspension has been developed recently for online monitoring in a flocculation system. In this paper, the authors tried to expand this technique to perform direct evaluation of floc size, settling velocity, and residual color after aluminum coagulation from the fluctuating light absorption using dual wavelengths. A theoretical study was carried out to establish the data handling algorithms for the evaluation of the above mentioned values from the fluctuating light absorbance. Two specific wavelengths were selected at near infrared and ultraviolet regions in order to characterize suspended matters and soluble colored organics. The usefulness of the proposed theory was verified in a series of batch coagulation tests with a newly developed dual wavelength photometric dispersion analyzer (DPDA). With an improved high precision photometer and data processing circuits, the extent of color colloid removal can be estimated at the beginning stage of coagulation/flocculation. The algorithms for the evaluation of floc size were calibrated and verified in flocculation experiments with micro photography. Flocculation and sedimentation experiments showed that settling velocity was successfully estimated by the proposed algorithms.

KEYWORDS

Coagulation, Flocculation, Floc size, Color removal, Monitoring, Dual wavelength, Absorption, Scattering

INTRODUCTION

In rapid filtration systems, the coagulation and flocculation processes should be properly designed and effectively operated for the solid-lquid separation process which follows. The dosages of chemicals in the flash mixer are the key factors which

control the coagulation process. The automatic control of dosage is normally carried out by a feedforward method on the basis of empirical data, or a feed back method based on the data of effluent quality from the solid liquid separation process, e.g. sedimentation.

This kind of feed forward control system assumes that historical data which the operators collect for plant operation is optimal, and cannot be directly applied to other water plants which treat different quality of raw water or use a different type of treatment system. Therefore, beyond the limit of the empirical relationship, it is necessary to rely on a jar test of raw water simulating coagulation, flocculation, and sedimentation. The feed back control system has a disadvantage that there is a long time delay between changes in raw water quality or chemical dosage and the corresponding effect on final water quality. Finally, a feed forward control method for chemical dosage based on coagulation theory is desirable, but has not yet come into practice. This is due to the fact that the relationship between water quality and optimal chemical dosage is difficult to derive theoretically, because a number of water constituents have an influence on the effect of chemical treatment.

Recent approaches to coagulation control consist of the online measurement of characteristics of microfloc generated just after chemicals are dosed. If measured micro floc characteristics give reliable information for solid liquid separation performance, a quick feed back system of coagulation control becomes possible. There are currently two prospective measurement methods considered to be useful. One is Streaming Current Monitor or Detector, SCM or SCD, based on the result that streaming current is proportional to electric mobility of flocs [1, 2, 3]. The other is Photometric Dispersion Analyzer, PDA, based on Gregory's theory that turbidity fluctuations in flowing suspension give a sensitive indication of floc growth [5, 6, 7, 8]. Matsui and Tambo proposed a floc size calculation equation from the PDA output by incorporating Tambo's floc density function into Gregory's PDA theory [9, 10, 11]. In the PDA, a single wavelength in near infrared region is used to detect the extent of agglomeration of suspended particles.

The objective of this research is to develop an online sensor to evaluate various characteristics of flocs formed at the beginning stage of coagulation in a rapid mixing tank. The research started from expanding the theory of PDA to simultaneous measurements of the extinction of plural wavelengths in the same light beam, and studying theoretically the characteristics of fluctuating extinction by absorbing and scattering substances which flow through the cell. This article focuses on the theoretical aspect of the technique and laboratory verification. Detail of the instrument and photometer developed on the theory is presented in the other articles [12, 13, 14]. Results of continuous in-situ monitoring by field application type equipment in flocculation basin will be described in another paper [14].

FLUCTUATION OF ABSORBANCE

As a suspension flows through a cell, light absorbance shows random fluctuation because of instantaneous variations of particle numbers in the cell for reasons discussed by Gregory [8]. For uniform suspension, mean values of fluctuating absorbances are expressed in terms of average numbers of particles, particle size, and a nondimensional scattering coefficient.

$$E_M = \nu \frac{\pi Q d^2}{4A} \quad (1)$$

where,
A : cross-sectional area of the light beam (cm^2)
d : diameter of suspended particle (cm)
E_M : average value of fluctuating absorbance (-)
Q : light scattering coefficient (-)
ν : average number of particles in the light beam (-)

Root mean square (RMS) values of fluctuating absorbance about the mean values correspond to standard deviations of varying particle numbers in the cell, as shown in equation (2).

$$E_{RMS} = \sigma \frac{\pi Q d^2}{4A} \quad (2)$$

where,
E_{RMS} : root mean square of fluctuating absorbance about mean value (-)
σ : standard deviation of fluctuating particle numbers about mean in the light beam (-)

Since local variation in composition of a suspension follows the Poisson distribution, the standard deviation about mean is equal to the square root of the average value.

$$\sigma = \nu^{1/2} \quad (3)$$

Therefore, combining equations (1) and (2) gives equation (4).

$$\frac{E_{RMS}}{E_M} = \nu^{-1/2} \quad (4)$$

Fig. 1 shows absorption spectra of kaolin suspension and peat water containing humic substances. In general, absorption (scattering) in a near infrared region is caused mainly by light blockages of suspended particles such as clays and flocs. On the other hand, ultraviolet light is sensitively absorbed by soluble humic substances as well as scattered by suspended particles.

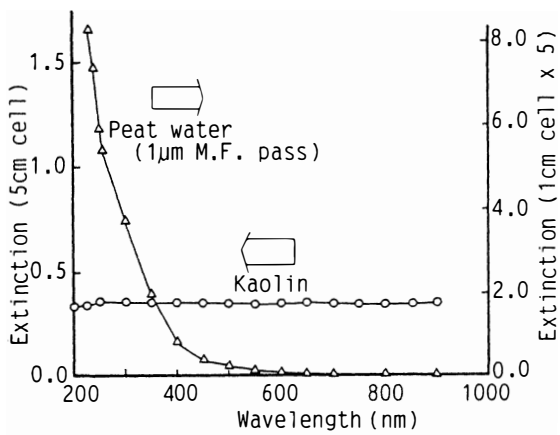

Fig. 1 Absorption Spectra of Kaolin Suspension and Peat Water

Therefore, mean values of light adsorption in the two wavelengths of near infrared and ultraviolet regions are written by equation (5) and (6), respectively.

$$E_{M1} = \nu \frac{\pi Q_1 D_F^2}{4A} \tag{5}$$

$$E_{M2} = \nu \frac{\pi Q_2 D_F^2}{4A} + E_{S2} \tag{6}$$

where,
D_F : floc diameter (cm)
E_{M1} : average absorbance for near infrared light (-)
E_{M2} : average absorbance for ultraviolet light (-)
E_{S2} : absorbance for ultraviolet light caused by soluble substances (-)
Q_1 : scattering coefficient of a floc for near infrared light (-)
Q_2 : scattering coefficient of a floc for ultraviolet light (-)

It should be noted, however, that absorption fluctuations are attributed only to suspended matters, irrespective of wavelength. Therefore, RMS values of fluctuating components are described for near infrared and ultraviolet regions, as follows.

$$E_{RMS1} = \nu^{1/2} \frac{\pi Q_1 D_F^2}{4A} \tag{7}$$

$$E_{RMS2} = \nu^{1/2} \frac{\pi Q_2 D_F^2}{4A} \tag{8}$$

where,
E_{RMS1} : root mean square of fluctuating absorbance about mean for near infrared light (-)
E_{RMS2} : root mean square of fluctuating absorbance about mean for ultraviolet light (-)

The corresponding expressions to equation (4) are as follows.

$$\frac{E_{RMS1}}{E_{M1}} = \nu^{-1/2} \tag{9}$$

$$\frac{E_{RMS2}}{E_{M2}-E_{S2}} = \nu^{-1/2} \tag{10}$$

FLOC SIZE

Theory of Floc Size Calculation

From equations (5), (6), and (8), we can derive two equations with respect to suspended particle size.

$$D_F = \sqrt{\frac{4AE_{RMS1}^2}{\pi Q_1 E_{M1}}} \tag{11}$$

$$D_F = \sqrt{\frac{4AE_{RMS1}E_{RMS2}}{\pi Q_2 E_{M1}}} \tag{12}$$

If the scattering coefficient is known, particle size can be calculated by only the average and RMS values of the fluctuating light absorbance.

Experimental Methods and Materials

Batch coagulation and flocculation tests were carried out for the evaluation of scattering coefficients of flocs and verification of equation (11) and (12). Wavelengths are selected at 860 nm and 253 nm. Fig. 2 illustrates the arrangement of DPDA, i.e.

dualwavelengthphotometric dispersion analyzer, and other apparatuses used in the jar tests. Using a flat flow pump, a suspension in a 5 L tank was circulated at the rate of 100 mL/min through the flowcell of DPDA. The effect of floc breakage by circulation through the pump is negligibly small. Details of DPDA are presented in the other reports [12, 13, 14].

Aluminum sulfate or PACl (poly-aluminum chloride) was used as a coagulant to coagulate kaolin suspension and diluted peat water which was pretreated by 0.2 μm membrane filtration. During the flash mixing of 100 rpm, an injection of aluminum was given preceding an injection of caustic soda to adjust pH. Following 2.5 min of flash mixing, the suspension was flocculated for 20 min at 40 rpm. The mixing intensity i.e. G value of flash mixing and slow mixing were 45 s^{-1} and 11 s^{-1}, respectively. The DPDA measurement and photographic observation of flocs were performed throughout the flash mixing and slow mixing durations. Photographic negatives were projected on the digitizer mat which connected with a personal computer, and an average size of flocs was analyzed.

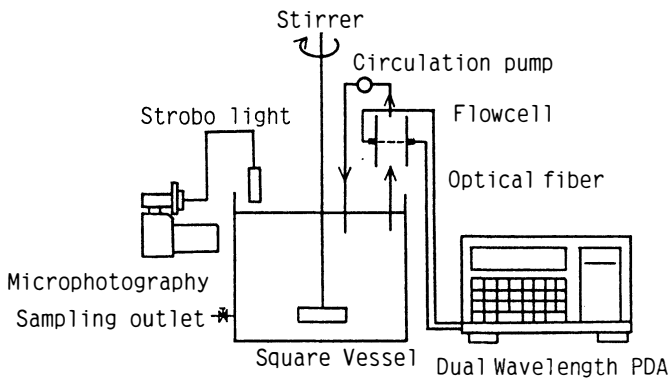

Fig. 2 Experimental Apparatus

Results

In a series of jar tests, the light scattering coefficients of flocs were evaluated by the comparison of photographically measured mean floc diameters with the processed DPDA outputs according to the equation (11) and (12), as shown in Fig. 3 and 4, respectively. The coagulation conditions of each experimental data in the figures are presented in Table 1. The ratio of numbers in ordinate to abscissa in the figures indicates the square root of scattering coefficients of flocs. From Fig. 3, the scattering coefficient with respect to near infrared light, Q_1, was distributed in a wide range of values with various ratios of aluminum dosages over turbidity (ALT ratio). The scattering coefficient with respect to ultraviolet light, Q_2, didn't change significantly with coagulation condition such as the ALT ratios or the existence of humic substances as shown in Fig. 4. These observed results can be explained as follows. Clay particles scatter near infrared light, but aluminum hydroxide is almost transparent. On the other hand, ultraviolet light is sensitive to both aluminum hydroxide and humic substances, as well as clay particles. Accordingly, the equation (12), substituting 0.24 for Q_2 which was evaluated by the regression line of

Fig. 4, is proposed as a simple floc size calculation equation.

Fig. 5 shows floc size variations with elapsed time through rapid and slow mixing stage in jar tests. A close agreement between measured floc size on photographs and calculated one by the equation (12) was obtained.

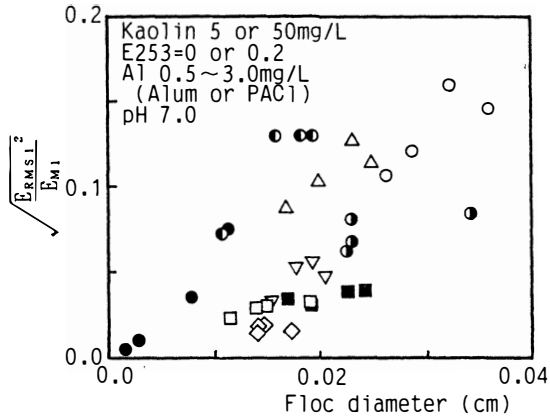

Fig. 3 Plots of DPDA Outputs against Floc Diameter for the Evaluation of Light Scattering Coefficients at 860 nm

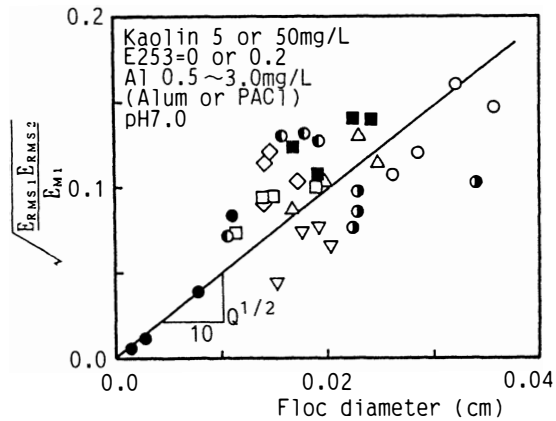

Fig. 4 Plots of DPDA Outputs against Floc Diameter for the Evaluation of Light Scattering Coefficients at 253 nm

Table 1 Experimental Conditions of Fig. 3 and 4

Symbol	Kaolin Conc. (mg/L)	UV Extinction (253nm, 1cm cell)	Al Conc. (mg/L)	Coagulant	pH
○	50	0.0	2.5	PACl	7
◐	50	0.0	0.5	PACl	7
◑	5	0.0	2.5	PACl	7
●	5	0.0	0.5	PACl	7
◇	0	0.2	3.0	PACl	7
□	5	0.2	2.5	PACl	7
■	5	0.2	5.0	PACl	7
△	50	0.0	2.5	Alum	7
▽	5	0.0	2.5	Alum	7

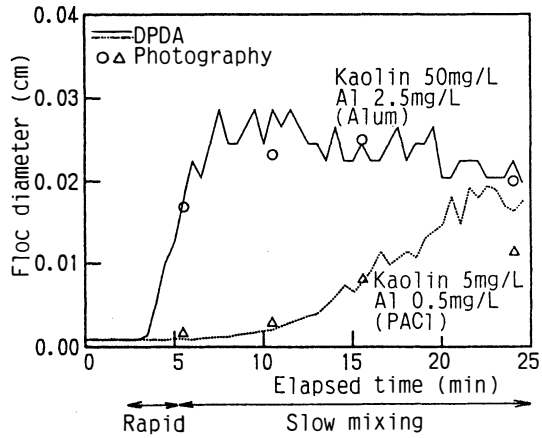

Fig. 5 Variation of Floc Diameter as a Function of Mixing Time

COLOR REMOVAL

Theory for Measuring Concentration of Uncoagulated Colored Organics

The removal of colored organic substances improves as aluminum dosage increases. Some parts of the organic substances are coagulated to generate flocs responding to a coagulant dosage. The rest of the organics still remain in solution. Floc number concentration can be expressed on the near infrared or ultraviolet absorption as shown in equations (9) or (10). By combining these equations, ultraviolet absorbance caused by uncoagulated parts of organics is given by equation (13).

$$E_{S2} = E_{M2} - E_{M1}\frac{E_{RMS2}}{E_{RMS1}} \qquad (13)$$

Verification

Jar tests with DPDA measurements were conducted in order to verify the applicability of the abovementioned theory. The suspension was prepared from kaolin clay blended in peat water. Duration time, rotational speed, and G value of rapid and slow mixing are 2.5 min, 100 rpm, 81 s^{-1} and 20 min, 30 rpm, 13 s^{-1}, respectively. After the slow mixing period, the uncoagulated parts of the sample were prepared by two kinds of solid liquid separation methods; 30 min settling, membrane filtration which has nominal pore size of 12 μm. The concentration was analyzed in UV extinction at 253 nm.

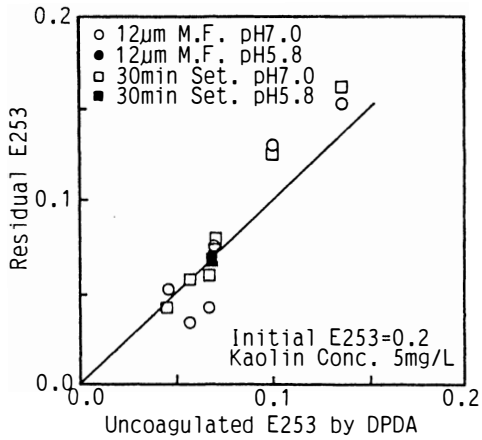

Fig. 6 Comparison of Uncoagulated E253 Analyzed with DPDA with Residual E253 Measured by Membrane Filtration or Settling

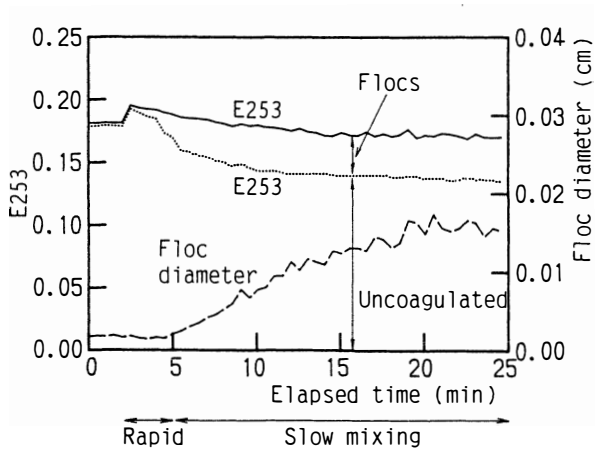

Fig. 7 Changes of Floc Diameter and E253 Analyzed with DPDA with Mixing Time

Results

Fig. 6 shows a relationship between ultraviolet absorbance of uncoagulated organics calculated by equation (9) on the DPDA outputs obtained at the end of a flocculation stage, and ultraviolet absorbance of settled or filtered samples. A good linearrelationship, as shown in Fig. 6 indicates the validity of equation (13). Typical observations of changes in floc size calculated by equation (12) and ultraviolet absorbance relating to uncoagulated humic substances by equation (13) throughout rapid and slow mixing in a jar test are shown in Fig. 7, 8, and 9. By the time floc growth reaches a maximum level, ultraviolet absorbance indicating the concentration of uncoagulated organics almost reaches an equilibrium state. This means that the residual concentration of colored organics after coagulation/flocculation and sedimentation can be evaluated on a DPDA measurement of a dosed suspension in the early stage of the reaction.

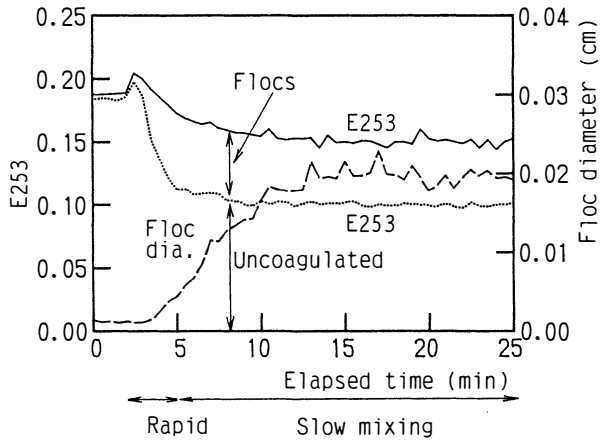

Fig. 8 Changes of Floc Diameter and E253 Analyzed with DPDA with Mixing Time

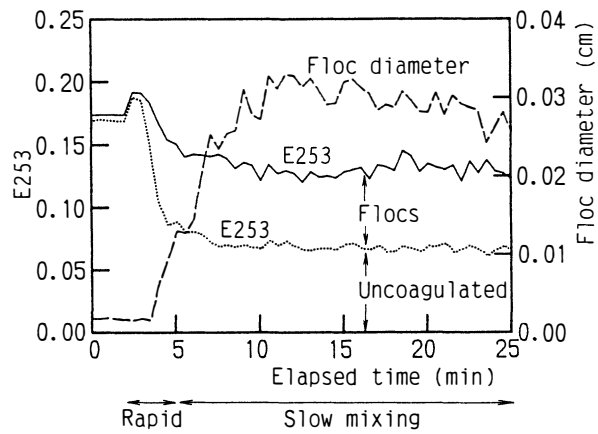

Fig. 9 Changes of Floc Diameter and E253 Analyzed with DPDA with Mixing Time

SETTLING RATE OF FLOCS

Derivation of Equation

An expression for the estimation of settling velocity of flocs can be derived by substituting equation (11) and a mass balance equation of a floc into the Stokes equation, and by some experimental information, as following procedures. Settling velocity of a floc depends on the size and density. The buoyant density of a floc is approximately expressed by equation (15), assuming the floc consists mainly of clay and aluminum.

$$W_F = \frac{\rho_{\bullet} g}{18\mu} D_F^2 \tag{14}$$

$$\frac{\rho_{\bullet}}{q_f} = \frac{\rho_{\bullet \cdot K}}{\rho_K} + R_{ALT}\frac{\rho_{\bullet \cdot A}}{q_A} \tag{15}$$

where,
W_F : settling velocity of a floc (cm/s)
g : gravitational acceleration coefficient (cm/s^2)
μ : viscosity of water (g/cm s)
$\rho_{\bullet}$: buoyant density of a floc (g/cm^3)
q_f : content of original suspended particles per unit volume of floc (g/cm^3)
ρ_K : density of suspended particles (g/cm^3)
$\rho_{\bullet \cdot K}$: buoyant density of suspended particles (g/cm^3)
$\rho_{\bullet \cdot A}$: buoyant density of hydrolyzed aluminum (g/cm^3)
q_A : aluminum content per unit volume of hydrolyzed aluminum (g/cm^3)
R_{ALT} : concentration ratio of aluminum over suspended particle (-)

Substituting equation (9), (11), and (15) into equation (14), followed by some algebraic manipulations relating to floc number concentration yields equation (16) and (17) for the settling velocity of a floc.

$$W_F = \frac{gLA^{1/2}}{6\pi^{1/2}\mu} P \frac{C_K}{E_{M1}}\left(\frac{E_{RMS1}^2}{E_{M1}}\right)^{1/2} \tag{16}$$

$$P = \left(\frac{\rho_{\bullet \cdot K}}{\rho_K} + R_{ALT}\frac{\rho_{\bullet \cdot A}}{q_A}\right) Q_1^{1/2} \tag{17}$$

where,
L : optical path length (cm)
C_K : concentration of clay particles (g/cm^3)

Experimental data shown in Table 2 with the scattering coefficients of flocs and kaolin and aluminum hydroxide properties suggests that the P in the equation (16) can be treated as constant [10, 11].

As light absorption in near infrared region was caused substantially by suspended matter such as clay particles, C_K/E_{M1} should be almost constant. Finally, equation (16) reduced to equation (18), substituting constants relating the experimental equipment and conditions.

$$W_F = 0.6\sqrt{\frac{E_{RMS1}^2}{E_{M1}}} \tag{18}$$

A similar expression to equation (17) was derived from the theory of photometric dispersion analyzer and floc density function [11, 15].

Table 2 Evaluation of P in Equation (16) as a function of ALT ratio

ALT ratio	$P = \left(\frac{\rho_{e,K}}{\rho_K} + R_{ALT}\frac{\rho_{e,A}}{Q_A}\right) Q_1^{1/2}$
0.005	0.51
0.01	0.48
0.02	0.45
0.05	0.43
0.1	0.45
0.2	0.51
0.5	0.66
1.0	0.78

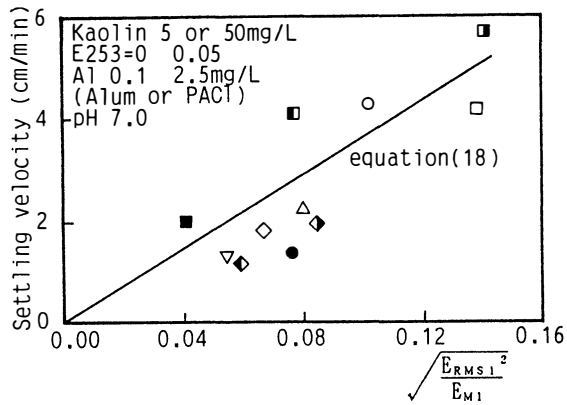

Fig. 10 Comparison of DPDA Outputs with 50% Settling Velocity of Flocs on the Cumulative Frequency Curve

Table 3 Experimental Conditions of Fig. 10

Symbol	Kaolin Conc. (mg/L)	UV Extinction (253nm, 1cm cell)	Al Conc. (mg/L)	Coagulant	pH
□	50	0.00	2.50	PACl	7
◨	50	0.00	0.50	PACl	7
◧	50	0.00	0.25	PACl	7
■	50	0.00	0.10	PACl	7
◇	5	0.00	2.50	PACl	7
◆	5	0.00	0.50	PACl	7
◆	5	0.00	0.35	PACl	7
○	50	0.05	1.00	PACl	7
●	5	0.02	2.50	PACl	7
△	50	0.00	0.50	Alum	7
▽	5	0.00	0.50	Alum	7

Experimental Method

Experimental verification was conducted with apparatuses and equipment shown in Fig. 1. Mixing conditions and materials used are the same as the experiments of floc size measurements described previously. After the flocculation period, settling velocity distribution of flocs was analyzed by incremental method. Samples were drawn from 3 cm below the vessel bottom at appropriate set intervals, and kaolin concentrations of drawn samples were measured. The 50% velocity on the cumulative frequency curve was used as representative settling velocity of flocs.

Results

Experimental data are plotted in Fig. 10, with the processed outputs of DPDA according to equation (18) as abscissa and the measured settling velocity of flocs as ordinate. The chemical conditions of each point of data in the figure are presented in Table 3. The straight line in the figure shows relationship calculated by equation (18). The plot shows that the relationships between measured values and calculated values on DPDA outputs are well represented by equation (16), irrespective of various chemical conditions.

CONCLUSION

Fluctuating absorbance analysis with near infrared and ultraviolet light is a good monitoring method of floc size and settling velocity, and good evaluation method of the concentration of uncoagulated colored organics as well.

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