

TURBIDITY REMOVAL FROM CLAY SUSPENSIONS BY USE OF ORGANIC POLYMERIC FLOCCULANTS

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Turbidity removal from clay suspensions by use of organic polymeric flocculants was studied by relating the change in floc size, optical density through a flocculation tank and amount of flocculant adsorbed onto suspended particles. Turbidity removal is represented by taking two regimes into consideration, i.e., the earlier period, appearing just after flocculant injection, when the flocculant adsorption rate controls the process, and the later period when a limited number of flocs named "mother flocs" control the process. The turbidity removal rates in both regimes were evaluated easily from the modified optical density variation proposed in this work and represented by two different first-order processes with respect to the modified optical density. The rate constants in both regimes were related linearly to each other, and its proportional constant depended on the condition of agitation.

Introduction

The removal of suspended substances from wastewater, i.e., turbidity removal by use of flocculants and/or coagulants, is one of the fundamental operations in water treatment. Organic polymeric flocculants have been used extensively in turbidity removal operations since the required amount of such flocculants is extremely small compared with that of inorganic coagulants. Although there have been many studies concerning the effects of flocculant properties and operational conditions on turbidity removal,^{1,2,4,9)} considerable experience is still required for the operations because no evaluation method for turbidity removal rate has been established. Turbidity removal results from the settling of flocs. Therefore, turbidity removal proceeds through a series of processes, i.e., the adsorption of flocculant molecules onto suspended solids and the floc growth process.^{5,6)} It is necessary to make clear the turbidity removal processes in order to evaluate the turbidity removal rate.

In the present work, turbidity removal from clay suspensions by use of organic polymeric flocculants is discussed. The process was evaluated by optical density, measured by a photometric device installed on a flocculation vessel, and related to both the changes of floc size and the amount of flocculant adsorbed.

1. Experiments

1.1 Materials

The clay suspensions and the organic polymeric flocculants used are shown in **Table 1**.

1) Clay suspensions Kaolin suspensions and silt suspension were used as model clay suspensions and a model turbid wastewater, respectively. The suspended particle size was less than 2 μm .

Kaolin (Fisher Scientific Co., K-5) suspensions were prepared using sodium hydroxide as a dispersant by the same method as reported elsewhere.⁴⁾

Silt was sampled from the campus of Tokyo Institute of Technology at Nagatsuta and ground in a mortar after drying. Silt suspension was prepared in the same manner as the preparation of kaolin suspensions, using 3×10^{-6} mol/m³ sodium hexametaphosphate as a dispersant.

2) Organic polymeric flocculants Nonionic polyacrylamide flocculant (Hokutan Kasei K.K., #100) and cationic polyacrylester flocculant (Diafloc Co., Kp-005) were used. Mean molecular weights of these flocculants are shown in Table 1.

1.2 Experimental apparatus and procedures

1) Flocculation tank A cylindrical vessel of 115 mm diameter and 150 mm height with six baffle plates of 10-mm width was used as a stirred tank. A six-bladed flat turbine impeller of 50-mm or 70-mm diameter was placed at a height of 30 mm from the bottom.

Flocculant solution of 0.01 dm³ volume and desired concentration was injected instantaneously by syringe into a suspension of 1 dm³ volume and a solid con-

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Table 1. Experimental materials

Suspensions		
Material		pH
Kaolin		10.5
Kaolin		7.5
Silt		6.0
Concentration, 250 g/m ³ ; particle size, less than 2 μm.		
Flocculants		
Material	Ionic state	Molecular weight
Polyacrylamide	Nonionic	4.87×10^6
Polyacrylamide	Nonionic	3.53×10^6 *
Polyacrylester	Cationic	1.00×10^6

* Prepared by the same method as reported elsewhere.⁴⁾

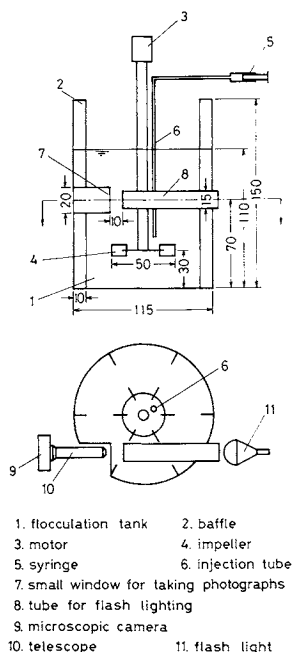


Fig. 1. Experimental apparatus for observation of floc size.

centration of 250 g/m³, stirred beforehand at a desired agitation speed. The flocculant injection point was in the vicinity of the impeller.

2) Observation of floc size Floc size was observed photographically. For photographing flocs a small window was made on the tank wall facing a tube of 15 mm diameter for flash lighting, as shown in **Fig. 1**. After the injection of flocculant, photographs of flocs were taken at desired intervals by a microscopic camera.

3) Measurement of optical density The device for measuring optical density is shown in **Fig. 2**. Three sets of photometric measurement systems were installed on the tank. CdS photocells and a fluorescent lamp were used as photometric detectors and light

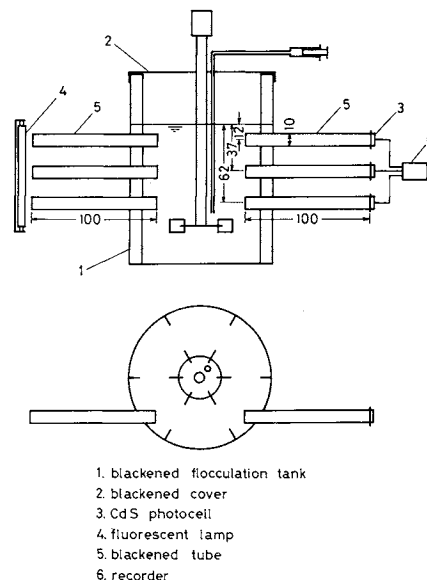


Fig. 2. Experimental apparatus for measurement of optical density.

source, respectively. The optical path length was 70 mm.^{*1}

After the injection of flocculant, changes in output voltage of photocells accompanying with light intensity variation due to flocculation were measured. Output voltage of the photocell was calibrated with optical density at a wave length of 800 nm with a spectrophotometer (Hitachi Co., type 124) using kaolin suspension as a standard suspension.

4) Measurement of amount of flocculant adsorbed
After flocculant injection, a sample suspension of 0.02 dm^3 volume including flocs was taken out of the tank at a desired time interval and centrifuged for 30 minutes at a rotational speed of 50 s^{-1} . The residual flocculant concentration in a centrifuged supernatant was measured by the method reported by Ootani *et al.*³⁾ The amount of flocculant adsorbed was calculated from the difference in amounts between injected and residual flocculant.

2. Experimental Results and Discussion

2.1 Floc size, optical density and amount of flocculant adsorbed

Figure 3 shows an example of floc size change obtained in the system of kaolin and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$). A large number of micro flocs came in sight about 30 seconds after flocculant injection (Fig. 3b). Floc size increased rapidly with time to about $150 \mu\text{m}$ at 240 seconds (Fig. 3d), and then gradually increased to $200 \mu\text{m}$ in average at 360 seconds (Fig. 3e). According to the change as seen in

*¹ It was confirmed that light intensity was proportional to optical path length over a wide range of suspended solid concentration.

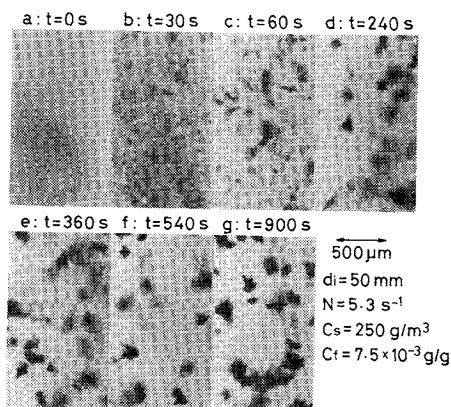


Fig. 3. Example of observation result of floc size change for kaolin (pH=10.5) and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$).

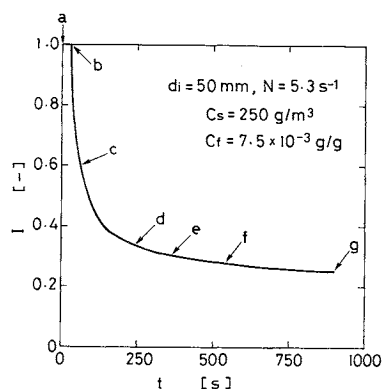


Fig. 4. Example of optical density variation under same conditions shown in Fig. 3.

Fig. 3, the number density of flocs decreased. After 360 seconds no remarkable changes of floc size or floc number density were observed (Fig. 3e–g), although the actual size of the flocs seemed to be distributed over a wider range.

Figure 4 shows the optical density change under the same experimental conditions shown in Fig. 3. The optical densities measured at three different axial positions at the same time lie one upon another. Accordingly, all solid particles including flocs must have been distributed uniformly through the tank. The optical density is normalized by the initial optical density as $I = I_t/I_0$. Up to about 30 seconds the optical density remained constant (Fig. 4a, b). Sakurai *et al.*⁷⁾ found a similar phenomenon for a coagulation and named it “waiting time.” After then the optical density decreased rapidly with time (Fig. 4b–d), and the rate of decrease became slow (Fig. 4d–g).

From the above result, it is considered that the optical density depended on the increase of floc size and the decrease of floc number density. In the region where the optical density decreased remarkably (Fig. 4b–d), rapid floc growth due to the coalescence of micro flocs was seen. In the subsequent region (Fig. 4e–g), changes of floc size and floc number density

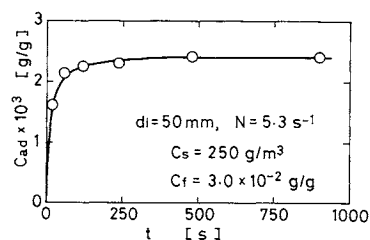


Fig. 5. Example of variation in amount of flocculant adsorbed for kaolin (pH=10.5) and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$).

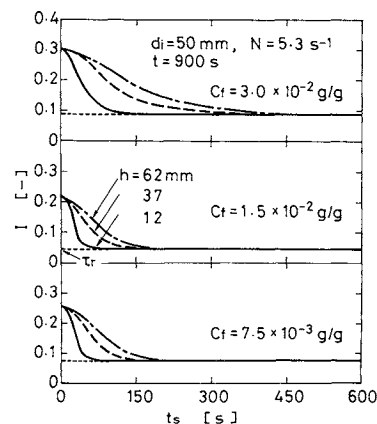


Fig. 6. Optical density variation during sedimentation for kaolin (pH=10.5) and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$).

were scarcely seen.

Figure 5 shows an example of amount of flocculant adsorbed onto the suspended solids obtained in the system of kaolin and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$). The amount adsorbed increased rapidly just after flocculant injection. After then the rate of increase of amount adsorbed became low with time, and in a short time no further increase was observed. Similar behavior was seen for a different flocculant dosage, and the adsorption rate just after flocculant injection increased with increase of flocculant dosage. What is expected on comparing the changes of floc size and flocculant adsorption amount is that the flocculant adsorption rate may affect the growth of floc just after flocculant injection.

2.2 Definition of residual turbidity

To evaluate the turbidity removal rate, the definition and physical meanings of residual turbidity must be made clear. **Figure 6** shows examples of optical density changes for three different flocculant dosages measured at three different axial positions during sedimentation. Just after discontinuing agitation, the optical density at any position decreased rapidly, accompanied by the settling of large flocs. The rate of decrease for each position is different. In a short time, however, the optical density at any position reached the same value, and the value was constant during further settling, although the time required to reach a constant value depended on the

floculant dosage. Similar behavior of optical density was observed for different periods of agitation. These results suggest that the residual particles in the supernatant are primary particles and that the constant optical density obtained by sedimentation is a function of the residual primary particles. Therefore, in this work, this optical density is defined as residual turbidity to distinguish it from the optical density before sedimentation, and is designated by τ_r .

2.3 Evaluation of turbidity removal rate from optical density variation

1) Relationship between residual turbidity and optical density An example of the residual turbidity change is shown in Fig. 7. Residual turbidity at each point was obtained by the procedure mentioned above. The change of optical density is also shown in the figure. After about 900 seconds the difference between optical density and residual turbidity become constant. As stated in 2.1, the floc size in this region was relatively large and no remarkable change of either size or number density of these flocs was observed, as shown in the cases of "e" to "g" in Fig. 4. On the other hand, the residual turbidity was sufficiently low in this region so that the number density of residual primary particles was also sufficiently low. Considering the facts presented above, it is concluded that the optical density in this region is determined solely by the light intensity transmitted directly, and the difference between optical density and residual turbidity corresponds to a cross-sectional area shaded optically by these large flocs. Therefore, turbidity removal in the later period was the result of uptaking the residual primary particles onto the large flocs, called "mother flocs."

2) Turbidity removal rate in the later period When the mother flocs are formed, they consist of 70–90% of the initial primary particles within experimental limits. On the other hand, the water content of flocs is usually greater than 98%. Thus the volume of mother flocs is more than 300 times that of the residual primary particles. Therefore, the size of the mother floc is considered to be kept constant during the uptaking of residual particles. The removal rate of primary particles under this condition is expressed by the equation presented by Tambo.⁸⁾

$$-dn_p/dt = \alpha D_f^3 n_f n_p \quad (1)$$

where n_p and n_f are the number density of primary particles and mother flocs, respectively, D_f is the mean diameter of mother floc and α is a flocculation coefficient. Here, D_f and n_f are both constant under the fixed experimental condition. Assuming that the mother flocs are formed at time t_m and $n_p = n_m$ at that time, the number density of residual primary particles, n_p , in the region of $t \geq t_m$ is expressed as follows:

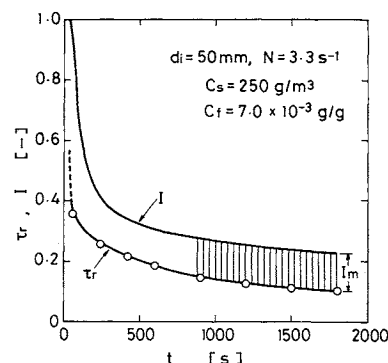


Fig. 7. Relationship between variations of optical density and residual turbidity for kaolin (pH=10.5) and polyacrylamide ($M_w = 4.87 \times 10^6$).

$$n_p = n_m \exp \{ -\alpha D_f^3 n_f (t - t_m) \} \quad (2)$$

The number density of residual primary particles is related to the residual turbidity as follows:

$$n_m/n_0 = \phi \tau_m, \quad n_p/n_0 = \phi \tau_r \quad (3)$$

where n_0 is the initial number density of primary particles, τ_m is the residual turbidity at $t = t_m$ and ϕ is constant. Substituting Eq. (3) into Eq. (2), the residual turbidity is expressed as follows:

$$\tau_r = \tau_m^* \exp (-\alpha D_f^3 n_f t) \quad (4)$$

where

$$\tau_m^* = \tau_m \exp (\alpha D_f^3 n_f t_m) \quad (5)$$

The relationship between optical density, I , and residual turbidity, τ_r , in the region of $t \geq t_m$ is given as follows:

$$\tau_r = I - I_m \quad (6)$$

where I_m is the constant defined in Fig. 7. The optical density, I , is modified by I_m as follows in order to evaluate the variation of residual turbidity from that of optical density:

$$I^* = (I - I_m)/(1 - I_m) = \tau_r/(1 - I_m) \quad (7)$$

and substituting Eq. (4) into Eq. (7), a modified optical density is expressed as follows:

$$I^* = I_m^* \exp (-\alpha D_f^3 n_f t) \quad (8)$$

where

$$I_m^* = \{ \tau_m/(1 - I_m) \} \exp (\alpha D_f^3 n_f t_m) \quad (9)$$

Equations (4) and (8) mean that the logarithms of residual turbidity and modified optical density decrease linearly with time in the region of $t \geq t_m$, and the slopes of the two straight lines are the same. Figure 8 shows the plots of $\log \tau_r$ and $\log I_m^*$ against time. The experimental results agreed well with Eqs. (4) and (8). Therefore, it is concluded that turbidity removal is a first-order rate process with respect to the modified

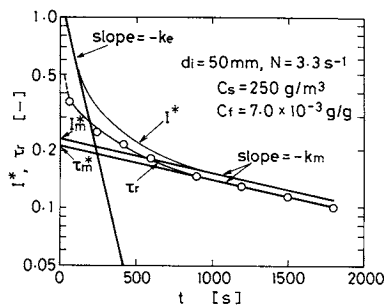


Fig. 8. Relationship between variations of modified optical density and residual turbidity plotted on semilogarithmic graph paper under same conditions shown in Fig. 7.

optical density. The rate constant k_m is expressed by $k_m = \alpha D_f^3 n_f$.

3) Definition of characteristic turbidity removal rate in the earlier region In the region where the floc size increased rapidly, no similar relationship between optical density and residual turbidity as described above was obtained. The modified optical density decreased linearly in the early stage of this region, as seen in Fig. 8. This slope, k_e , is conveniently defined as a characteristic rate constant of turbidity removal. **Figure 9** shows the relationship between k_e and flocculant dosage in the case of kaolin and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$). The characteristic constant, k_e , has a maximum with respect to flocculant dosage. This result supports the conclusion that the turbidity removal rate depends on the flocculant adsorption rate as stated in 2.1.

4) Relationship between rate constants, k_e and k_m It is confirmed that turbidity removal proceeds through a series of processes, i.e., floc size growth and uptaking of primary particles onto mother flocs, but these two are not independent of each other. **Figure 10** shows the relationship between the rate constants, k_e and k_m , obtained in systems of several kinds of clay suspensions and polymeric flocculants at the same agitation speed. The experimental conditions are shown in **Table 2**. The relationship is described by a straight line through the origin for all experimental conditions. Accordingly, the turbidity removal rate in the presence of mother flocs depended on the rate in the early stage where floc size increased remarkably.

In turbidity removal operations, it should be stressed that agitation should continue at least until mother flocs are formed, since the size of mother floc is usually large enough to settle out and the residual turbidity in the presence of mother flocs is sufficiently low. Therefore, mother flocs play important role with respect to turbidity removal. The turbidity removal rate in the presence of mother flocs is easily evaluated from the simple measurement of optical density variation.

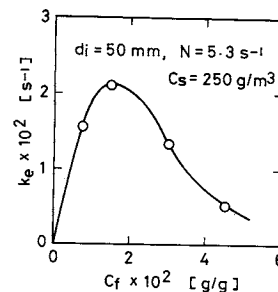


Fig. 9. Relationship between rate constant k_e and flocculant dosage for kaolin (pH=10.5) and polyacrylamide ($\bar{M}_w = 4.87 \times 10^6$).

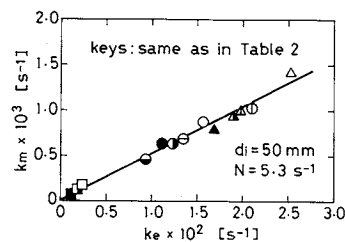


Fig. 10. Relationship between rate constants, k_e and k_m .

Table 2. Experimental conditions

Material	\bar{M}_w [—]	C_f [g/g]	N [s ⁻¹]	Key
Kaolin (pH=10.5) — Polyacrylamide	4.87×10^6	7.5×10^{-3}	5.3	⊙
		15.0×10^{-3}		○
		30.0×10^{-3}		⊖
	3.53×10^6	15.0×10^{-3}	5.3	●
		30.0×10^{-3}		⦿
Kaolin (pH=7.5) — Polyacrylester	1.00×10^6	5.0×10^{-3}	5.3	△
		15.0×10^{-3}		△
		25.0×10^{-3}		▲
		35.0×10^{-3}		▲
Silt (pH=6.0)	4.87×10^6	1.5×10^{-3}	5.3	■
		2.2×10^{-3}		□
		3.2×10^{-3}		□

$d_i = 50$ mm.

2.4 Effects of agitational speed on turbidity removal rate

Figure 11 shows the relationship between the rate constants, k_e and k_m , at two agitation speeds with a turbine impeller of 70 mm diameter. The experimental conditions are shown in **Table 3**. Although the rate constant k_m is proportional to k_e in the case of the same agitation speed, the proportional constant at the higher agitation speed is small compared with that at the lower. Accordingly, the proportional constant is a function of agitation conditions. The relationship between agitation speed and turbidity removal rate should be evaluated by taking the proportional con-

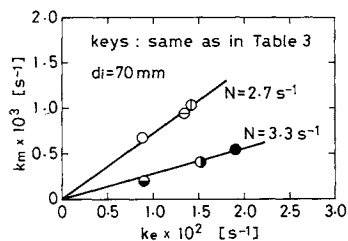


Fig. 11. Effect of speed of agitation on relationship between rate constants, k_e and k_m .

Table 3. Experimental conditions

N [s ⁻¹]	C_f [g/g]	Key
2.7	3.25×10^{-3}	○
	6.50×10^{-3}	⊙
	9.75×10^{-3}	⊖
3.3	3.25×10^{-3}	●
	9.75×10^{-3}	⊙
	13.0×10^{-3}	⊖
$d_i = 70 \text{ mm.}$		

stant into consideration. The evaluation of turbidity removal rate with the proportional constants will be useful in determining the agitation conditions in turbidity removal operations, although further studies are necessary.

Conclusion

Turbidity removal from clay suspension by use of organic polymeric flocculants is represented by taking two regimes into consideration. The first is the earlier period, just after flocculant injection. In this regime floc size increased rapidly. The turbidity removal rate in this regime is closely related to the rate of flocculant adsorption onto the suspended solids. In the second regime, large flocs called "mother flocs" are present. The size and the number density of mother flocs are almost constant through the period. Turbidity removal in this regime proceeded by an uptaking of primary particles onto the mother flocs.

The turbidity removal rates in both regimes are easily evaluated from the simple measurement of optical density variation and are represented by two different first-order processes with respect to the modified optical density proposed in this work. The rate constants in the two regimes are linearly related to each other, and the proportional constant depends on the agitation conditions.

In turbidity removal operations, it should be stressed that agitation should continue at least until mother flocs are formed.

Nomenclature

C_{ad}	= amount of flocculant adsorbed per unit weight of suspended solid	[g/g]
C_f	= flocculant dosage per unit weight of suspended solid	[g/g]
C_s	= concentration of suspended solid	[g/m ³]
D_f	= diameter of mother floc	[m]
d_i	= impeller diameter	[m]
h	= depth	[m]
I	= normalized optical density ($= I_t/I_0$)	[—]
I^*	= modified optical density defined by Eq. (7)	[—]
I_0	= initial optical density	[—]
I_m	= difference between normalized optical density and residual turbidity ($= I - \tau_r$)	[—]
I_m^*	= defined by Eq. (8)	[—]
I_t	= optical density at time t	[—]
k_e	= rate constant in the early stage	[s ⁻¹]
k_m	= rate constant in the presence of mother flocs	[s ⁻¹]
\bar{M}_w	= mean molecular weight of flocculant	[—]
N	= speed of agitation	[s ⁻¹]
n_0	= initial number density of primary particles	[m ⁻³]
n_f	= number density of mother flocs	[m ⁻³]
n_m	= number density of primary particles at $t = t_m$	[m ⁻³]
n_p	= number density of primary particles	[m ⁻³]
t	= duration of agitation	[s]
t_m	= time required to form mother floc	[s]
t_s	= settling time	[s]
α	= flocculation coefficient	[s ⁻¹]
τ_m	= residual turbidity at $t = t_m$	[—]
τ_m^*	= defined by Eq. (5)	[—]
τ_r	= residual turbidity	[—]

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