Effect of Intermittent Addition on Turbidity Removal by Polymer Flocculant: Computer Simulation of Simplified Flocculation Model

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Effect of Intermittent Addition on Turbidity Removal by Polymer Flocculant: Computer Simulation of Simplified Flocculation Model

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Since there are many factors which influence the process of flocculation by polymer flocculant, the scientific understanding of the flocculation mechanism is still under discussion. We have proposed a simple bridging model which expresses flocculation under various additive manners of the flocculant and enables the understanding of qualitative trends of the flocculation system. In the present study, from the simulated results based on the model and experimental data, we obtained the following knowledge: 1) the intermittent addition of polymer flocculant gives better and reproducible turbidity removal; 2) the optimum dosage, which results in maximum turbidity removal in a given manner of addition, increases as the number of doses under the intermittent addition increases; 3) at a given amount of primary particles, the reproducibility at the optimum dosage of the 1-time dose is the worst among all results, irrespective of the additive manner. It could, therefore, be concluded that all these findings are originating from the difference of probability of bridging formation among particles under various additive manners.

Introduction
Polymers are widely used in many industrial applications, e.g., water treatment, papermaking, etc. They can produce large and strong flocs which can easily be separated from the original suspensions by physical means (Gregory and Barany, 2011). There are many factors affecting flocculation of suspension by use of polymer flocculants, such as molecular weight of the polymer, its constituent monomer species and their combination, its concentration in a target colloidal system, the affinity between polymer and colloidal particles, and solution environment (pH, ionic strength, etc.) (Gregory, 1973; Ash and Clayfield, 1976; Higashitani and Kubota, 1987; Adachi et al., 1994; Hogg, 2013). Therefore, it is difficult to evaluate the actual flocculation process quantitatively. Several simulations for studying the dispersion/aggregation mechanism of nanoparticles in a polymer system using a molecular dynamics (MD) method have been reported (Liu et al., 2011; Patra and Singh, 2014). These simulations can be correctly illustrated for the system under a given simple condition (e.g., temperature, pressure, nanoparticle’s volume fraction, etc.), but they are far from enough to discuss the stability of the real colloidal dispersion. It is well known that the amount of polymer flocculant adsorbed onto colloidal particles profoundly affects the stability of the colloidal suspension (Fleer and Lyklema, 1974; Ash and Clayfield, 1976; Gregory and Barany, 2011). To explain the flocculation mechanism, several models of bridging between two or more particles by adsorbed polymers have been proposed (Smellie and La Mer, 1958; Healy and La Mer, 1964; Sakohara et al., 1980; Hogg, 1984; Moudgil et al., 1987; Molski, 1989; Elimelech et al., 1995). La Mer and co-workers (Smellie and La Mer, 1958; Healy and La Mer, 1964) expressed bridging flocculation in terms of the fraction of the surface covered by adsorbed polymer. This model can explain experimental results under limited conditions, e.g., low polymer concentration, the initial step of flocculation, etc. On the other hand, the engineered approach given by Sakohara et al. (1980) is based on the concept that both a polymer molecule and a suspended particle are assumed to have only two active sites through which they can be attached to each other; particles are joined linearly by bridging flocculation, resulting in a linear floc. This model enables us to understand the qualitative trends of the flocculation system.

In our previous study (Kadooka et al., 2017), we proposed an extension of Sakohara’s model which expresses flocculation under various additive manners of the flocculant and enables the understanding of qualitative trends of the flocculation system. Based on our experience, the turbidity removal and its reproducibility are much affected by dose conditions of polymer solution. To the best of our knowledge, however, reproducibility of turbidity removal by use of polymer flocculant has not been discussed yet in the literature. In this study, we simulated bridging flocculation using a revised Sakohara model. Based on the simulated and experimental results, we will discuss the effect of dose conditions (number of doses, polymer concentration, and dispersion state of polymer flocculant after its dosage to the colloidal suspension) on turbidity removal and its...
1. Model Simulation of Bridging Flocculation

1.1 Visualized one-dimensional flocculation model

Sakohara et al. (1980) simplified the three-dimensional configuration of polymer molecules and colloidal particles of their mixture in a real system to the linear combination of particles and polymer molecules. Following Sakohara’s definition of legend symbols, we proposed a simple bridging model in our previous study (Kadooka et al., 2017). We represented a polymer molecule by a straight line which has only two active sites at both ends, and a suspended particle by a circle which also has only two active sites on the opposite sides of its surface, as shown in Figure 1. The objective of this simplification is to represent the three-dimensional configuration of polymer molecules and primary particles in a real mixture with a one-dimensional combination of particles and polymer molecules as explained below.

We simplify the situation of bridging by polymer flocculant as shown in Figure 2. Flocculation by the polymer is assumed to occur in the case where only one polymer molecule exists between particles as indicated by the arrows in the figure. On the other hand, flocculation is assumed not to occur in the case where more than one polymer molecule exists between particles as indicated by the triangle in the figure. Once the relative position of particles and flocculant molecules is assigned, it is held unchanged to represent the unevenness of particle-flocculant mixture which depends on the manner of addition of flocculant. These rules of the flocculation model are based on some known facts such as: 1) a colloidal suspension is sometimes stabilized by the hydrophilic nature of polymer flocculant which excessively adheres to the particle surface (Fleer and Lyklema, 1974; Napper, 1977; Gregory and Barany, 2011); and 2) appearance of a lump of polymer flocculant leads to a decrease in bridging ability.

However, this model does not consider the following phenomena which are encountered in practice: 1) breakage of flocs; 2) changes in flocculation rate due to the growth of the flocs (Higashitani et al., 1978; Tambo and Watanabe, 1984); 3) changes in flocculation ability due to a combination of physical and chemical properties of particle and polymer; 4) changes in adsorption rate and adsorbed amount of polymer due to change of the flocculant morphology and its concentration (Black et al., 1966; Van de Ven, 1994; Aoki and Adachi, 2006; Gregory and Barany, 2011); and 5) flocculation by polymer flocculant other than bridging mechanism (Gregory, 1973; Gregory and Barany, 2011; Feng et al., 2015). Therefore, this model is restricted to systems where bridging is the predominant mechanism of flocculation.

Fig. 1 Simplification of bridging flocculation by polymer flocculant

Fig. 2 Distinction between flocculation and dispersion; bridging occurs at the positions indicated by the arrows and does not occur at the position indicated by the triangle

We evaluate the stability of colloidal suspension by the simplified model simulation as shown in Figure 3. Results of model simulation under several situations (i.e., the results simulated under several combinations among the number of primary particles \(N_0\), the number of polymer molecules \(P\), and the number of doses \(n\)) are shown in Figures 4 and 5. Figure 4(a) shows that the flocculation is terminated because of lack of flocculant molecules. The flocculation in Figure 4(b) is satisfactory because of an adequate amount of flocculant, while in Figure 4(c) particles remain suspended due to an excessive dose of flocculant. Thus, the model proves the existence of “an optimum dosage” of polymer flocculant. By adding an adequate amount of molecules in each step (described as “intermittent addition”), the stabilization of particles due to overdose would rarely arise as shown in Figure 5.

Fig. 3 Schematic illustration of the simplified flocculation simulation; if suspended particles and polymer molecules are aligned as shown in the upper diagram, they change to that shown in the lower diagram based on the rule shown in Figure 2

(a) Under dose \((P = 3)\)

(b) Adequate dose \((P = 11, \text{ near the optimum dosage})\)

(c) Overdose \((P = 28)\)

Fig. 4 Results of model simulation \((N_0 = 16)\) under various polymer doses
II. 1.2 Computer simulation of bridging flocculation

To obtain a better approximation to a real colloidal particle-polymer flocculant system, we used the computer simulation program written in C (run under Microsoft Visual C++ 2010 Express ver. 10.0). To evaluate turbidity removal, we define the threshold value for the number of settling particles $D_{sed}$ and relative turbidity $\tau$. We assume that the floc consisting of more than $D_{sed}$ primary particles settles out by gravity. Relative turbidity $\tau$ is defined by Eq. (1).

$$\tau = \frac{N_s}{N_0}$$  \hspace{1cm} (1)

Here, $N_s$ is the sum of primary particles and flocs which consist of less than $D_{sed}$ primary particles and remain suspended. We use the relative turbidity as a measure of turbidity removal. To make the computer program, we prepared the following subprograms.

I. Generation of random array (using the Mersenne twister algorithm (Matsumoto and Nishimura, 1998)) composed of suspended particles and polymer molecules

II. Distinction between flocculation and dispersion under the rule shown in Figure 2, and removal of large flocs which consist of more than or equal to $D_{sed}$ primary particles from the system

III. Insertion of polymer molecules between particles in random order

IV. Calculation of relative turbidity by counting the number of polymer molecules on average relative turbidity under various numbers of doses is indicated in Table 1. Based on the simulated results, the effect of the number of polymer molecules on average relative turbidity under various numbers of doses is indicated in Figure 7. It can be recognized from the figure that the intermittent addition of polymer flocculant leads to a dramatic decrease in relative turbidity. The figure also suggests that the intermittent addition increases the probability of bridging between neighboring particles. With increasing number of doses, the number of polymer molecules at which the minimum value of relative turbidity is observed (i.e., the optimum dosage, as shown by the arrows in Figure 7) increases. This result implies that polymer molecules are used more effectively under the intermittent addition. In the divided dose, since the number of polymer molecules in each dose is less than that of 1-time dose, the probability for the appearance of a situation where only one polymer molecule is assigned between two particles increases; this decreases the turbidity of the system at a given dose of flocculant. Figure 7 implies this increase of probability is more drastic in the high polymer dose region, resulting in the shift of the optimum point shown by the arrows. The effect of the number of polymer molecules on the variance of relative turbidity under 1-time / 100-times stepwise doses is depicted in Figure 8. Error bars in the figure represent ±3σ, where σ is the standard deviation of $N_s/N_0$. From the comparison between Figures 8(a) and 8(b), at the optimum dosage, the intermittent addition of polymer flocculant gives better and reproducible turbidity removal. Thus, it can be concluded that the number of polymer doses is responsible for the variation of turbidity removal at the optimum dosage. This phenomenon will be discussed again in Section 3.2. At much lower (or higher) dosages than the optimum dosage in Figures 8(a) and 8(b), the reproducibility of turbidity removal is better than that near optimum dosage in 1-time.

### Table 1: Input conditions for the flocculation simulation

<table>
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<tr>
<th>Number of primary particles</th>
<th>Number of polymer molecules</th>
<th>Number of doses</th>
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<td>$P$</td>
<td>$n$</td>
<td>$D_{sed}$</td>
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<td>1–200</td>
<td>4</td>
<td>Figures 15 &amp; 16</td>
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dose in Figure 8(a); this is because the relative turbidity does not exceed unity. The opposite trend is observed when the optimum turbidity approaches naught as shown in Figure 8(b) since the relative turbidity does not become negative. It should be noted that at a given number of primary particles, the reproducibility at the optimum dosage of the 1-time dose is the worst one among all results, irrespective of the additive manner. Even if the threshold value $D_{\text{sed}}$ is varied from 2 to 100, the number of polymer molecules at which the minimum value of average relative turbidity is observed (shown by the arrows in Figure 7) does not change; the average relative turbidity changes slightly depending on the threshold value as illustrated in Figure 9.

2. Experimental

Spherical PMMA particles of 0.4 µm in nominal diameter (MP-1000, Soken Chemical & Engineering Co., Ltd.) were used as the model suspended particles. The particles are highly monodispersed. A linear copolymer, acrylamide-2-(dimethylamino) ethyl-acrylate methyl chloride (DIAFLOC KP204BS, Mitsubishi Chemical Corp.), was employed as the flocculant. The structural formula of the copolymer is shown in Figure 10. The nominal molecular weight is 13 million. A stock solution of polymer flocculant was prepared with a concentration of 500 ppm and was used up within a period of a one week time. In a 1-time-dose.
experiment, 10 mL of the polymer flocculant solution was mixed with the same amount of colloidal suspension with a concentration of 2000 ppm in the test tube (25 mL). Mixing was carried out by end-over-end rotation with the frequency of 1 Hz for 30 s. In the \( n \)-times-stepwise-dose experiment, the 10 mL polymer solution was divided into \( n \) parts. Each part was mixed with the suspension according to the method mentioned above. Optical Density (OD) was measured after 300 s from the end of mixing operation using a spectrophotometer (U-2000A, Hitachi, Ltd., wavelength = 660 nm). Solutions of different concentrations of polymer flocculant, as shown in Table 2, were used in flocculation experiments. We restricted ourselves to the flocculation system where the bridging is the predominant mechanism of flocculation. The combination of negatively charged PMMA and cationic polymer flocculant KP204BS satisfies this condition. It is clear that the flocculation by charge neutralization does not occur in this situation since the sign of electrophoretic mobility of PMMA changes from negative to positive at a very small dose of KP204BS (ca. 0.03 ppm). Incidentally, the hydraulic radius of KP204BS in 0.1 M NaCl aqueous solution obtained from the conventional Huggins plot is 141 nm, and the radius in a salt-free condition determined by Pavlov’s method (Pavlov et al., 2006) is 289 nm, on the basis of the Einstein viscosity equation.

All experiments were conducted at room temperature (293 K) and ion-exchanged water (electroconductivity \( \sigma \approx 1 \) \( \mu \)S/cm) was used for each sample preparation. All measurements were carried out more than five times to confirm their reproducibility.

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**Fig. 9** Effect of threshold value \( D_{\text{sed}} \) on the variance of relative turbidity under 20-times stepwise dose (simulated results)

**Fig. 10** Chemical structure of the polymer used as a flocculant

\[
\begin{align*}
-\text{(CH}_2\text{-CH}_3)_n- & \quad -\text{(CH}_2\text{-CH}_2)_n- \\
\text{CONH}_2 & \quad \text{COO(CH}_2\text{)}_2\text{N}^{\text{+}}(\text{CH}_3)\text{Cl}
\end{align*}
\]

**Fig. 11** Effect of polymer flocculant dosage on the average value of relative turbidity (experimental results)

**Fig. 12** Effect of polymer flocculant dosage on the variance of relative turbidity under (a) 1-time dose and (b) 10-times stepwise dose (experimental results)
3. Results and Discussion

3.1 Comparison of the results of simulation and experiment

To describe the effect of turbidity removal, relative turbidity in this experiment is defined by Eq. (3).

$$\tau_{exp} = \frac{OD}{OD_{sus}}$$  \hspace{1cm} (3)

Here, OD was measured for each flocculation experiment and OD_{sus} is the optical density for a 1000 ppm PMMA suspension. Average relative turbidity (\(= OD_{exp} / OD_{sus}\)) is also defined by the arithmetic average of \(\tau_{exp}\).

Based on the experimental results, the effect of polymer flocculant dosage on the average value of relative turbidity is shown in Figure 11. The effect of polymer flocculant dosage on the variance of relative turbidity under each number of dosages is shown in Figure 12. Figures 11 and 12 show the same qualitative trends as suggested by the simulated results (Figures 7 and 8). The optimum dosage which results in the best turbidity removal increases as the number of doses increases as shown in Figure 11, in accord with the simulated results shown in Figure 7. Meanwhile, the experimental results under 1-time dose show the largest variance near the optimum dosage (25 ppm) as illustrated in Figure 12(a), corresponding to the simulated results in Figure 8(a). Therefore, the proposed model of bridging flocculation is useful to discuss the stability of real colloidal suspensions.

3.2 Statistical analysis of simulated results

We define the degree of dispersion \(S^2\) of primary particles and polymer molecules in the above simulation, which represents the deviation from a uniform conformation of polymer molecules, by the following equations.

$$S^2 = S_1^2 + S_2^2$$  \hspace{1cm} (4)

$$S_1^2 = \frac{1}{N+1} \sum_{k=0}^{N} (p_k - \frac{P}{N+1})^2$$  \hspace{1cm} (5)

$$S_2^2 = \frac{1}{P+1} \sum_{k=0}^{P} (n_k - \frac{N}{P+1})^2$$  \hspace{1cm} (6)

Here, \(N\) is the total number of primary particles and \(P\) is the total number of polymer molecules. \(S_1^2\) is the deviation from the uniform conformation of polymer molecules with respect to \(N+1\) positions, i.e., \(N\)-1 positions between \(N\) particles and both ends: the left position of the particle at the left end and the right position of the particle at the right end. \(S_2^2\) is the deviation from the uniform conformation of particles to the \(P+1\) positions, i.e., \(P\)-1 positions between \(P\) molecules of polymer flocculant and both ends: the left position of the molecule at the left end and the right position of the molecule at the right end. \(p_k\) in Eq. (5) is the number of polymer molecules between \(k\)th and \((k+1)\)th particles, and \(n_k\) in Eq. (6) is the number of particles between \(k\)th and \((k+1)\)th polymer molecules. The smaller value of \(S^2\) represents a good dispersion under a given combination of \(N\) and \(P\).

Figure 13 shows that the dispersion status affects the flocculation process. That is, a smaller degree of dispersion \(S^2\) gives better dispersion status. Figure 14 is a series of the simulated results classified according to \(S^2\) against final output data. In this figure, it is shown that the smaller value of \(S^2\) gives better turbidity removal. Moreover, with decreasing values of \(S^2\), the optimum dosage increases except for \(S^2 > 4\). The result shown in Figure 14 is similar to those of Figure 7 (simulation) and Figure 11 (experiment). Figure 15 shows that both the value of \(S^2\) and the average relative turbidity decrease with the number of doses. Therefore, it can be inferred that the intermittent addition is equivalent to minimizing the value of \(S^2\). As shown in Figure 16, we can consider the distribution of \(\ln S^2\) under various numbers of doses as the normal distribution. It can be seen from the figure that \(\ln S^2\)-distribution shifts to the left as the number of doses increases. This shift results in the improvement of turbidity removal, as shown in Figures 13 and 14. The decrease of the relative turbidity makes their variance smaller since they cannot be negative. Consequently, the number of doses is responsible for both the reproducibility and improvement of turbidity removal.

Although the proposed one-dimensional model is very simple, it follows the qualitative trend of the experiment under the condition where bridging is the predominant mechanism of flocculation. Quantitative simulation is not possible, however, since there is no fitting parameter in the model.

### Table 2 Experimental conditions for flocculation of PMMA suspension

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<tr>
<th>Concentration of suspension [ppm]</th>
<th>Concentration of polymer flocculant [ppm]</th>
<th>Number of doses</th>
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<td>1000</td>
<td>1, 5, 10, 25, 50, 100</td>
<td>1, 2, 5, 10</td>
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Fig. 13 Results of model simulation (\(N_0 = 10, P = 9\)) under the various dispersion

(a) Bad dispersion \((S^2 = 6.17)\)

(b) Good dispersion \((S^2 = 0.91)\)

(c) The best dispersion \((S^2 = 0.15)\)
Conclusions

In the present paper, we simulated bridging flocculation using the simplified one-dimensional flocculation model and considered the effect of turbidity removal of polymer flocculant on a few operating conditions (the number of doses, polymer concentration, and dispersion state). From the results of model simulation and experiment, the following conclusions are drawn: 1) the intermittent addition of polymer flocculant gives better and reproducible turbidity removal; 2) the optimum dosage which results in the best turbidity removal increases as the number of doses increases; and 3) at a given amount of primary particles, the reproducibility at the optimum dosage of 1-time dose is the worst among all results, irrespective of the additive manner. In addition, the statistical analysis of simulation results suggests that the number of doses is responsible for the possibility of the favorable configuration of polymer molecules.

Acknowledgement

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Literature Cited


Gregory, J.; “Rates of Flocculation of Latex Particles by Cationic Polymers,” J. Colloid Interf. Sci., 42,


