



The role of rapid mixing condition on picophytoplankton floc growth

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ABSTRACT

This work aims to evaluate the effect of different velocity gradient and rapid mixing time on floc properties of picophytoplankton, using polyaluminum chloride (PACl) and polysilicic acid (PSi) as coagulant. The growth, breakage, and re-growth of flocs were followed by a particle size analyzer in order to investigate the underlying mechanisms. Three different zones were found to be depending on G value in coagulation process. At low G value ($G < 200 \text{ s}^{-1}$), the aggregation dominated over breakup. At mean G_{values} ($G = 250 \text{ s}^{-1}$ for *Synechococcus* sp.-PSi flocs and $G = 546 \text{ s}^{-1}$ for kaolin-PSi flocs; $G = 200 \text{ s}^{-1}$ for *Synechococcus* sp.-PACl flocs and $G = 390 \text{ s}^{-1}$ for kaolin-PACl flocs) flocs formation was maximized, producing the largest flocs. For large G values ($G > 250 \text{ s}^{-1}$ for *Synechococcus* sp.-PSi flocs and $G > 546 \text{ s}^{-1}$ for kaolin-PSi flocs; $G > 200 \text{ s}^{-1}$ for *Synechococcus* sp.-PACl flocs and $G > 390 \text{ s}^{-1}$ for kaolin-PACl flocs), breakup dominated over floc formation. Broken flocs did not fully re-grow after breakage; however, the re-growth rate of *Synechococcus* sp. flocs was larger than that of kaolin flocs, probably as a result of the surface properties of *Synechococcus* sp. The rapid mixing time of 60 and 90 s led to maximum floc formation *Synechococcus* sp. and kaolin systems, respectively.

Keywords: Velocity gradient; Rapid mixing time; Picophytoplankton; Floc formation and breakage; Turbidity removal

1. Introduction

Coagulation is one of the most important processes used for removing suspended particles in water treatment plants. The coagulation process is influenced by coagulant type and dosage, particle property and concentration, solution pH, velocity gradient, and dura-

tion [1]. Especially, the interparticle collision frequency and growth of aggregates and the uniformly dispersion of hydrolyze product of coagulants depend on the velocity gradient (G) and duration [2,3].

Several researchers have found that velocity gradient and rapid mixing time influence the coagulation process. Rossini et al. [4] found that the rapid mixing

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time had a significantly influence on coagulation efficiency. Although a short rapid mixing time provided the lowest values of residual turbidity, prolonged rapid mixing time gave poorer performance. Vrale and Jorden [5] suggested that instant rapid mixing time below 1 s performed the best coagulation efficiency. Mhaisalkar et al. [6] obtained similar conclusions, although the effects of rapid mixing conditions were rather small. Previous studies on velocity gradient also showed optimum condition. G value of 350 s^{-1} was found to give minimum residual turbidity and the lowest concentration of small particle (below $2\text{ }\mu\text{m}$). With a much lower G value (25 s^{-1}), flocs growth grew more slowly and reached smaller sizes [7]. Colomer et al. [8] investigated the aggregation and breakup of particle flocs under low velocity gradient (from 0.70 to 27.36 s^{-1}) and that there was an increase of floc size at increasing G values. Furthermore, Zhan et al. [3] found three different zones which were depending on G values in the coagulation process. At low G values, the mean particle diameter increased with G values and the aggregation dominated over breakup. At intermediate G values, flocculation rates were maximized, which produced the largest flocs. For large G values, breakup dominated over aggregation. In the last case, an increase in the shear rate caused a reduction in the mean particle size.

Picophytoplankton is a small plankton ranging between 0.2 and $2\text{ }\mu\text{m}$ in size, comprised of picocyanobacteria and eukaryotic phototroph [9]. The presence of picophytoplankton and its metabolites in the drinking water source can cause a series problems for drinking water treatment. For instance, picophytoplankton cells contributed to the turbidity of treated water and clog the filters in the facilities. Their intracellular metabolites also contributed to the production of undesired tastes and odors, and the formation of assimilable organic carbon (AOC), disinfection byproducts (DBPs) and various other toxins [10,11]. The influence of picophytoplankton and its intracellular metabolites on water quality and human health was first reported in the 1980s. Faust and Aly [12] reported that picophytoplankton affected the water colour and gave it a musty or fishy odor. Nakamura et al. [13] and Hoson et al. [14] showed that picoplankton, especially picophytoplankton, contributed to the turbidity of treated water. In addition, Domingos et al. [15] reported that picoplanktonic cyanobacteria contribute to microcystin produce and picoplanktonic cyanobacteria species behaves much like other microcystin-producing cyanobacterial species with regard to poison. Carmichael and RenHui [16] reported that picophytoplankton *Synechococcus* produces microcystin which can cause liver disease in human beings.

To date, numerous studies have tried to find optimum velocity gradient and mixing time for the inorganic and organic systems. However, the nature of the contaminants varies and all water sources contain picophytoplankton which has the different surface and floc properties than organic and inorganic systems. Therefore, the aim of this study is to determine the effect of different velocity gradient and rapid mixing duration on floc growth of picophytoplankton system in order to improve the coagulation–flocculation process.

2. Materials and methods

2.1. Preparation of kaolin suspension

Kaolin clay was used as the model suspension (Kanto Chemical, Japan). Five grams of kaolin was dispersed completely in 500 mL distilled water with a high speed blender. After bleeding, the kaolin suspension was made up to 1 L and allowed to stand for 24 h to allow for complete hydration of the kaolin. The stock solution was diluted with tap water to adjust the sample turbidity to 10 NTU . The alkalinity was adjusted to 35 mg/L as CaCO_3 by adding NaHCO_3 . The diluted synthetic water samples were kept in reservoirs at room temperature before use.

2.2. Coagulants

polyaluminum chloride (PACl) and polysilicato-iron (PSI) were obtained from Kanto Chemical Co. Inc. and Suido Kiko Kaisha Ltd., respectively. Stock solutions with PACl and PSI were prepared in distilled water.

2.3. Cultivation and preparation of *Synechococcus* sp. suspension

Cyanobacterium *Synechococcus* sp. strain (NIES-1348) was obtained from National Institute for Environmental Studies (NIES) in Japan and cultivated in axenic CB medium at $25\pm 1^\circ\text{C}$ under fluorescent light ($18\text{ }\mu\text{mol photons/m}^2/\text{sec}$, $12\text{-h light}/12\text{-h dark}$). The CB medium was composed of $15\text{ mg C Ca (NO}_3)_2\cdot 4\text{H}_2\text{O}$, 10 mg KNO_3 , $5\text{ mg }\beta\text{-Na}_2\text{ glycerophosphate. } 5\text{H}_2\text{O}$, $4\text{ mg MgSO}_4\cdot 7\text{H}_2\text{O}$, $0.01\text{ }\mu\text{g Vitamin B}_{12}$, $0.01\text{ }\mu\text{g Biotin}$, $1\text{ }\mu\text{g Thiamine HCl}$, $50\text{ mg Tris (hydroxymethyl) aminomethane}$, $0.3\text{ mg/L Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, $0.0588\text{ mg/L FeCl}_3\cdot 6\text{H}_2\text{O}$, $0.0108\text{ mg/L MnCl}_2\cdot 4\text{H}_2\text{O}$, $0.0031\text{ mg/L ZnSO}_4\cdot 7\text{H}_2\text{O}$, $0.0012\text{ mg/L CoCl}_2\cdot 6\text{H}_2\text{O}$, and $0.00075\text{ mg/L Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$. pH of the medium was adjusted by

adding either 0.1 M NaOH or 0.1 M HCl. *Synechococcus* was grown in a 200 ml Erlenmeyer flask at unialgal level with 100 ml of CB medium on a rotary shaking device (90 rpm). The cell populations were measured by counting at least 100 cells in triplicate using a light microscope. The cells in the stationary phase of culture were served and diluted with tap water to a population concentration of approximately 1.8×10^6 .

2.4. Zeta potential measurements

The zeta potential measurements were obtained using a Micro-Electrophoresis Apparatus Mk II (Rank Brothers, UK). The zeta potential was evaluated at a room temperature of $20 \pm 1^\circ\text{C}$ and in suspension under an applied electric field of 80 mV. The zeta potential was calculated according to the Smoluchowski equation.

2.5. Standard jar test and rapid mixing

Jar testing of kaolin and picophytoplankton (*Synechococcus* sp.) systems was conducted with a high speed jar test apparatus with four paddle-stirrers (60 mm \times 30 mm). Paddles and shafts were made of stainless steel in Technical Division in Tohoku University. Jar test procedure comprised a 3 min rapid mixing at 150 rpm for addition of varying coagulant doses and subsequent pH adjustment using the appropriate amounts of HCl and NaOH to pH 6.5 for *Synechococcus* sp. and pH 7.0 for kaolin. This was followed by a 30 min flocculation period at 30 rpm and settling period of 60 min. After settling, samples were taken from 2 cm below the surface for measurements. The residual turbidity of the supernatant was measured once the specimen had settled. The zeta potentials of the suspensions were also measured via a zeta analyzer.

Rapid mixing experiments were performed with the same mixing device. Rapid mixing according to the changes of velocity gradient and mixing time was conducted to investigate the growth of flocs in each condition. Rapid mixing speeds were changed in the range from 100 rpm ($\sim 20 \text{ s}^{-1}$) to 1,600 rpm ($\sim 1,110 \text{ s}^{-1}$) and mixing times were changed in the range from 30 s to 180 s. Flocs growth rate and the average floc size after the rapid mixing were analyzed by particle size analyzer (Microtract ASVR, HRA X-100, Nikkiso, Japan).

3. Results

3.1. Coagulant dosage optimization

Optimum coagulant dose for kaolin suspension was determined through standard jar tests. Several PSI

and PACl dosages, ranging from 10 to 50 mg/L, were applied to coagulate the kaolin suspension. The zeta potential of the kaolin particles in the suspension and the residual turbidity after mixing and settling are shown in Fig. 1. Through jar testing procedure, it showed that the coagulant dose giving the maximum turbidity removal efficiency for PSI was 30 mg/L; whilst the corresponding value for PACl was 40 mg/L. At those coagulant doses, the zeta potential of the kaolin suspension was nearest to zero. Residual turbidity increased gradually at the PSI dose over 30 mg/L and PACl dose over 40 mg/L, due to restabilization by charge reversal of particles. From these results, the optimum dosage of PSI and PACl was determined to 30 and 40 mg/L, respectively.

Jar test experiments were also conducted for *Synechococcus* sp. suspension. The zeta potential of *Synechococcus* sp. was measured in order to determine the optimal coagulant dose of PSI and PACl. The coagulant doses giving the zeta potential nearest zero were selected as optimum coagulant dose. Accordingly, the optimum coagulant dose of PSI and PACl was determined to 140 and 200 mg/L, respectively (Fig. 2).

3.2. Effect of velocity gradient and time

3.2.1. The floc property of *Synechococcus* sp. system

In order to determine the effect of G values as well as rapid mixing time for growth properties of kaolin and *Synechococcus* sp. suspension with PSI and PACl, floc size during rapid mixing was analyzed in the range of G value from 100 rpm ($\sim 20 \text{ s}^{-1}$) to 1,600 rpm ($\sim 1,110 \text{ s}^{-1}$) and mixing time from 30 to 180 s, respectively. The floc size is represented by mean particle diameter (d_{50}) and the results were in Fig. 3. For

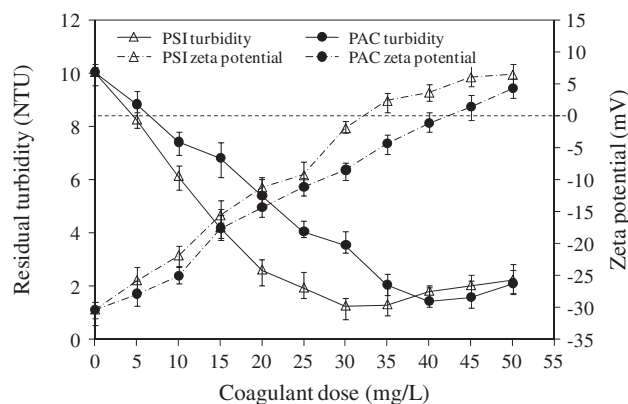


Fig. 1. Effect of coagulant dose on residual turbidity and zeta potential.

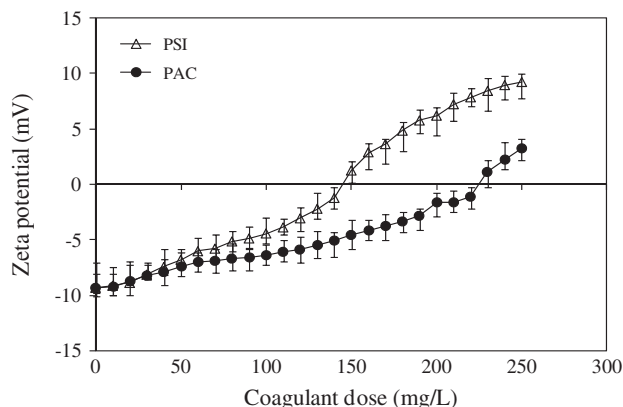


Fig. 2. Effect of coagulant dose on zeta potential of *Synechococcus* sp.

Synechococcus sp.-PSI flocs, d_{50} reached a maximum size ($238.8\mu\text{m}$) at G 250 s^{-1} and mixing time of 90 s. When G value over 250 s^{-1} and mixing time over 90 s formed, d_{50} was decreased as a result of floc breakage. Through the breakage period, *Synechococcus* sp.-PSI floc size changed from 238.8 to $174.3\mu\text{m}$ when G value was increased from 250 to 320 s^{-1} . Following the breakage period, there is only partial recovery of d_{50} , showing that the broken *Synechococcus* sp.-PSI flocs can only re-grow to a limited extent. In this period, the flocs size increased from 174.3 to $197.2\mu\text{m}$ again when G value was increased from 320 to $1,110\text{ s}^{-1}$. It is likely that this effect can be explained by the much higher collision rate between *Synechococcus* sp. cell and hydroxide flocs during the rapid mixing phase [17]. However, d_{50} after the breakage period was always lower than those before breakage, which is typical of flocs formed with hydrolyzing coagulants under sweep coagulation condition [18,19].

For *Synechococcus* sp.-PACI flocs, d_{50} reached a maximum size at G 200 s^{-1} ($159.2\mu\text{m}$) and mixing time of 60 s. Through the breakage period, *Synechococcus* sp.-PACI flocs size changed from 159.2 to $94.5\mu\text{m}$ when G value was increased from 200 to 250 s^{-1} (Fig. 3). Following the breakage period, d_{50} increased again by increasing G value. The trend of re-growths of *Synechococcus* sp.-PACI flocs was similar to *Synechococcus* sp.-PSI flocs. However, the size of re-growth flocs and the strength of *Synechococcus* sp.-PSI flocs to high shear were higher than *Synechococcus* sp.-PACI flocs under the same experiment conditions. The re-growth properties of *Synechococcus* sp.-PSI flocs could be explained by the better bridge formation capability of PSI between the broken flocs. As it is known that the activated silica improved bringing properties of PSI [20], and thus PSI could be brought together the broken flocs better than PACI. Therefore, the re-

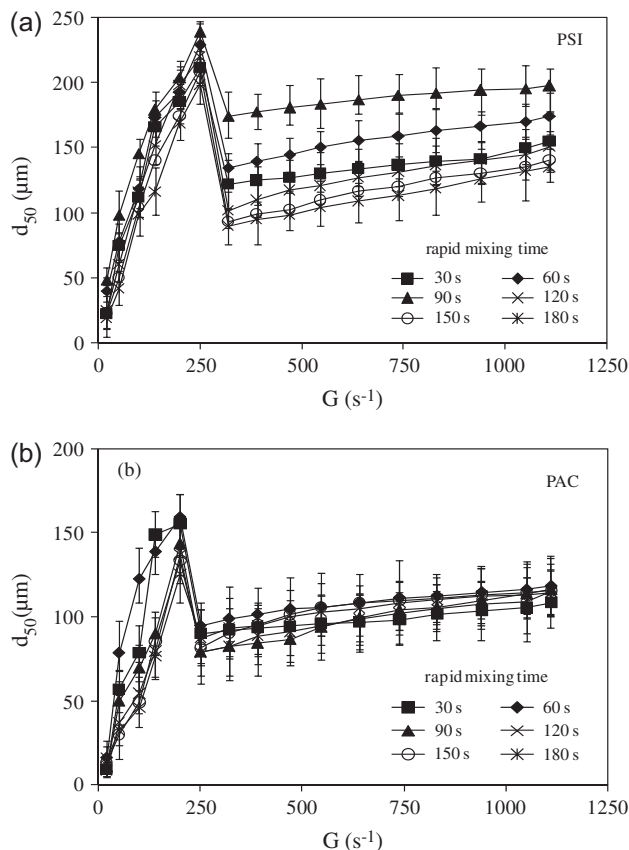


Fig. 3. (a) *Synechococcus* sp. floc size formed by PSI and (b) PACI under various G values.

growth rate and size of *Synechococcus* sp.-PSI flocs were larger than *Synechococcus* sp.-PACI. In addition, the strength of *Synechococcus* sp.-PSI flocs to high shear may be attributed to the larger size of *Synechococcus* sp.-PSI flocs and the making of strong bonds of PSI. Therefore, it should be pointed out that the re-growth of flocs was controlled not only by G value but also by the characteristics of different coagulants. Similar observations have been reported previously for PACI–natural organic matter (NOM) and polyferic chloride (PFC)–NOM flocs. In that study, the results showed that PFC–NOM flocs had higher strength to higher G value (200 s^{-1} for 1 min) compared to PACI–NOM flocs [3].

Fig. 4(a) shows the effect of rapid mixing time on the evolution of *Synechococcus* sp.-PSI flocs size distribution at G value of 250 s^{-1} which results in maximum d_{50} . At mixing time of 30 s, the medium and large size flocs started to form. After mixing time of 60 s, the medium size flocs turn to the large size flocs. The evolution of *Synechococcus* sp.-PSI flocs reached a maximum particle size distribution of 10.85% by

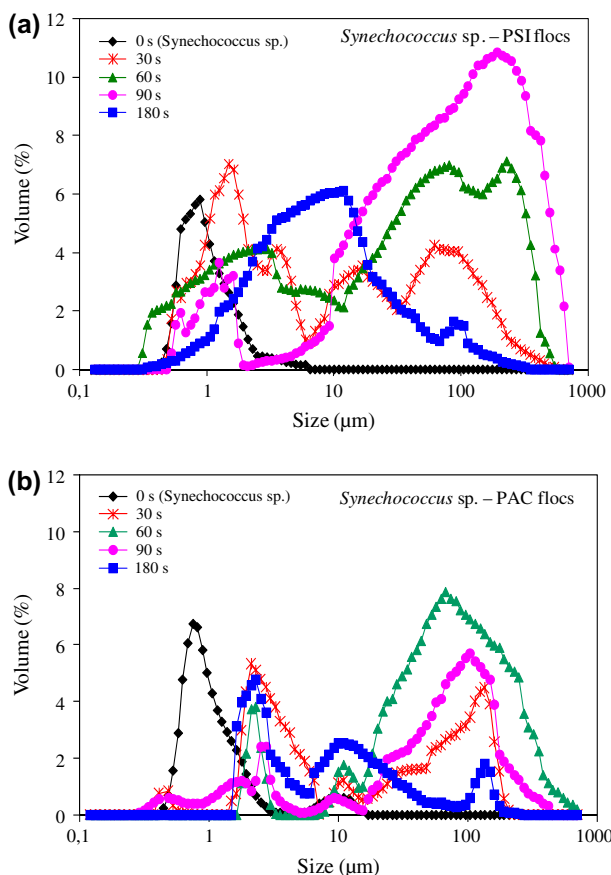


Fig. 4. (a) *Synechococcus sp.*-PSI and (b) *Synechococcus sp.*-PACI floc size distribution for different rapid mixing times (volume (%): percentage of total particles).

mixing time of 90 s, which is corresponded with larger size flocs (100–1,000 μm).

After mixing time over 90 s, the volume of *Synechococcus sp.*-PSI flocs started to decrease due to the breaks of larger size floc. It shows that the longer exposure (over 90 s) to high shear causes the breakage of *Synechococcus sp.*-PSI flocs. As a result, the optimum rapid mixing condition for *Synechococcus sp.*-PSI flocs can be suggested as mixing time of 90 s at G value of 250 s^{-1} .

The *Synechococcus sp.*-PACI flocs size distribution at G value of 200 s^{-1} is shown in Fig. 4(b). It can be seen that the major peak was observed at the mixing time of 60 s and the volume of *Synechococcus sp.*-PACI flocs reached to the particle size distribution of 8.87%. The major peak shifted to a smaller value as the increase of mixing time over 60 s. At the mixing time of 180 s, almost all of the largest size flocs (100–1,000 μm) were broken due to longer mixing time therefore, smaller and middle size flocs started to increase again. It can be suggested that for the maxi-

imum growth of *Synechococcus sp.*-PACI flocs, the maximum floc volume of 60 s was required.

As a result, the result of velocity gradient and rapid mixing time experiments showed that the *Synechococcus sp.*-coagulant floc size reached to maximum at the mean velocity gradient of 200 and 250 s^{-1} with a rapid mixing time between 60 and 90 s, respectively. Therefore, the mean velocity gradient with the short rapid mixing period may be suggested for the treatment of picophytoplankton-contaminated water in drinking water treatment plant.

3.2.2. The floc property of kaolin system

Fig. 5 shows kaolin-PSI flocs formation with different velocity gradient. Kaolin-PSI flocs reached to a steady-state floc size between G value of 200 and 546 s^{-1} with mixing time of 60 s. d_{50} value of kaolin-PSI flocs reached a maximum size (347.6 μm) at G 546 s^{-1} with mixing time of 60 s which is corresponded with the lowest residual turbidity. When G value over 546 s^{-1} and mixing time over 60 s formed,

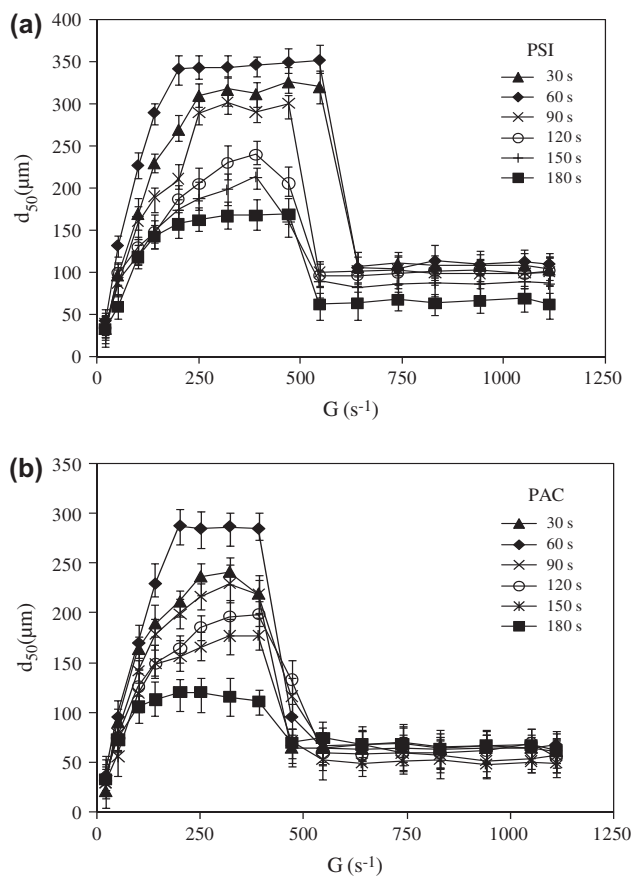


Fig. 5. (a) Kaolin floc size formed by PSI and (b) PACI under various G values.

d_{50} was significantly decreased as a result of floc breakage. Through the breakage period, kaolin-PSI floc size changed from 347.6 to 105.3 μm when G value was increased from 640 to 1,110 s^{-1} . Following the breakage period, kaolin-PSI floc was slightly re-grown from 105.3 to 113.3 μm . The re-growth rate of kaolin-PSI flocs was very low compare to *Synechococcus* sp.-PSI flocs. These observations indicated that kaolin-PSI floc had relatively high ability to withstand shear in the jar tester compare to *Synechococcus* sp.-PSI flocs. However, *Synechococcus* sp.-PSI flocs had relatively high re-growth ability than kaolin-PSI floc after the breakage period.

Fig. 5(b) shows kaolin-PACl flocs formation with different velocity gradient. d_{50} value of kaolin-PACl flocs reached a maximum size (287.5 μm) at G 200 s^{-1} with the rapid mixing time of 60 s. The size of kaolin-PACl flocs was almost same between G value 200 and 390 s^{-1} . At G value over 390 s^{-1} , kaolin-PACl flocs size significantly decreased from 284.6 to 63.4 μm . The

re-growth rate of kaolin-PACl flocs was very low as it was in kaolin-PSI experiments. In addition, the results also showed that floc formed by PSI was much strength to shear compare to floc formed by PACl.

Fig. 6 shows the effect of rapid mixing time on the kaolin-PSI flocs size distribution at G value of 470 s^{-1} . The volume of kaolin-PSI flocs reached a maximum particle size distribution of 12.87% by mixing time of 60 s. In rapid mixing time over 60 s, the volume of kaolin-PSI flocs decreased to maximum particle size distribution of 8.89% while the flock breakage occurs with rapid mixing time of 180 s. It is observed that longer mixing time would result in break of large flocs.

Similar results were also obtained for kaolin-PACl flocs (Fig. 6(b)). However, the maximum volume of kaolin-PACl was slightly lower compare to that of kaolin-PSI. The volume of kaolin-PACl flocs reached a maximum particle size distribution of 10.56% by mixing time of 60 s. Therefore, rapid mixing time of 60 s

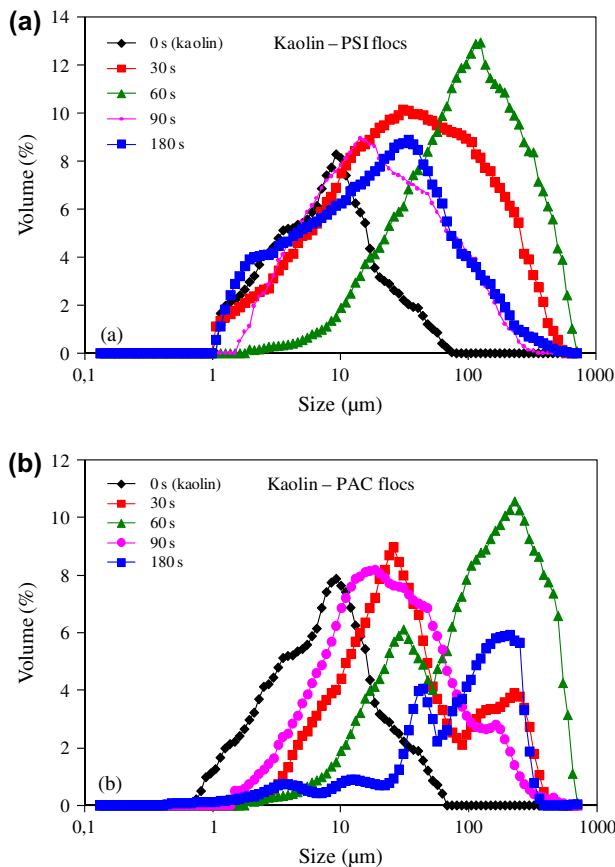


Fig. 6. (a) Kaolin-PSI and (b) kaolin-PACl floc size distributions for different rapid mixing times (volume (%): percentage of total particles).

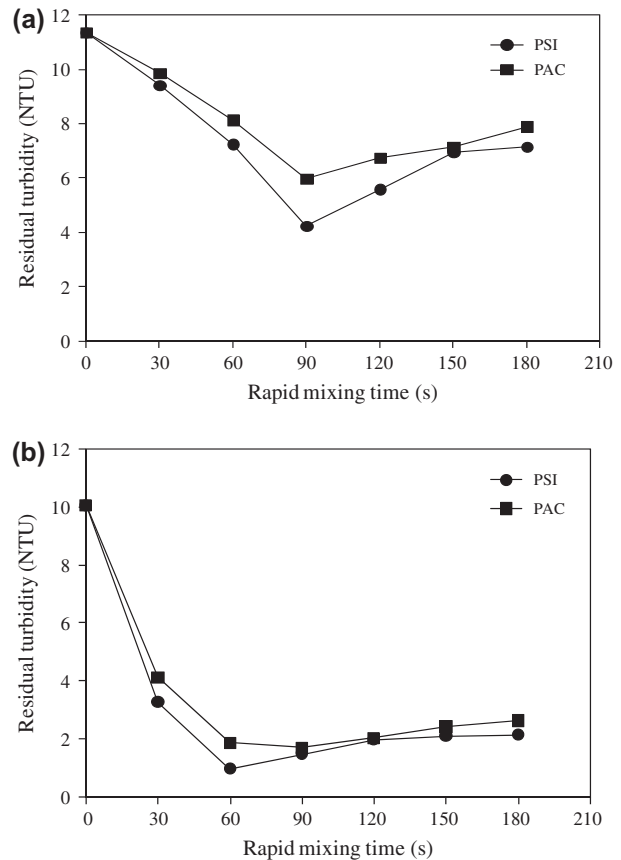


Fig. 7. (a) Effect of rapid mixing time on residual turbidity in *Synechococcus* sp. (initial turbidity: 11.35 NTU, G 250 s^{-1} and 140 mg/L PSI, G 200 s^{-1} and 200 mg/L PACl) and (b) in kaolin suspension (initial turbidity: 10.05 NTU, G 470 s^{-1} and 30 mg/L PSI, G 390 s^{-1} and 30 mg/L PACl).

may be recommended to make larger flocs for both kaolin-PSI flocs and kaolin-PACl flocs.

3.3. Effect of mixing time on turbidity removal

Residual turbidity after jar tests with *Synechococcus* sp. and kaolin suspension were monitored to confirm the effects of mixing time on turbidity removal. Fig. 7 shows the turbidity removal through rapid mixing time each time after slow mixing for flocculation and sedimentation sequentially. For *Synechococcus* sp. suspension, at G value of 250 s^{-1} and PSI dose of 140 mg/L , residual turbidity decreased gradually to 4.23 NTU , as rapid mixing time increased to 90 s . On the other hand, residual turbidity increased at rapid mixing time over 120 s . In addition, at a G value of 200 s^{-1} and PACl dose of 200 mg/L , residual turbidity was 5.98 NTU , as rapid mixing time increased to 60 s . Residual turbidity increased again with rapid mixing time over 90 s as it was in PSI.

Fig. 7(b) shows the turbidity removal of kaolin suspension. A G value of 470 s^{-1} is corresponded maximum d_{50} and PSI dose of 30 mg/L , residual turbidity decreased to 0.96 NTU with rapid mixing time of 60 s . At a G value of 390 s^{-1} and PACl dose of 40 mg/L , residual turbidity of kaolin suspension decreased to 1.69 NTU , as rapid mixing time increased to 60 s .

The results showed that the formation of large flocs in rapid mixing step affected the turbidity removal in each system after sedimentation, which might affect the flocculation and sedimentation efficiencies. In addition, the optimum rapid mixing time depends on the many factors such as G value, the content of suspension, and the characteristics of coagulant.

4. Discussions

The coagulation experiments were conducted in order to characterize the floc formation ability of picophytoplankton and kaolin system. We compared the share resistance of *Synechococcus* sp.-coagulant and kaolin-coagulant flocs in different rapid mixing condition with PSI and PACl. In the literature, there are rather contradictory recommendations for rapid mixing parameters. Some authors suggest instantaneous mixing based on contact-destabilization theory, whereas others recommend mixing time of few minutes [4,21].

In this study, it was noted that the floc size of both *Synechococcus* sp. and kaolin system first increased and then decreased with the increased G in the coagulation process, which demonstrated that there were

three different ranges for both *Synechococcus* sp. and kaolin flocs formation: low velocity gradient ($G < 200\text{ s}^{-1}$), which was the aggregation-dominated range; mean velocity gradient ($G = 250\text{ s}^{-1}$ for *Synechococcus* sp.-PSI flocs and $G = 546\text{ s}^{-1}$ for kaolin-PSI flocs; $G = 200\text{ s}^{-1}$ for *Synechococcus* sp.-PACl flocs and $G = 390\text{ s}^{-1}$ for kaolin-PACl flocs), where coagulation rates were maximized and breakup minimized; and high velocity gradient ($G > 250\text{ s}^{-1}$ for *Synechococcus* sp.-PSI flocs and $G > 546\text{ s}^{-1}$ for kaolin-PSI flocs; $G > 200$ *Synechococcus* sp.-PACl flocs and $G > 390\text{ s}^{-1}$ for kaolin-PACl flocs), where flocs breakup dominated. In the aggregation-dominated range, aggregates size increased in proportion to the share rate, but resulted in small floc sizes that were limited by low particle collision rates. Although breakup probably occurred, it was considered relatively insignificant to the overall aggregate sizes. In the mean velocity gradient, the balance between the rate of aggregation and the rate of breakage was reached; the flocs reached the maximum size. In the breakup-dominated range, there were sufficient collisions to produce flocs. In the beginning of this range, while the floc size of *Synechococcus* sp. slightly decreased the floc size of kaolin, system significantly decreased. It was observed that the *Synechococcus* sp. flocs had less breakup in comparison to kaolin flocs. At the end of this range, it was observed that the re-growth ability of *Synechococcus* sp. flocs was higher than that of kaolin flocs.

The velocity gradient range used in this study slightly was higher than that in previously studies. Nevertheless, the velocity gradient giving the largest floc formation for both picophytoplankton and kaolin system was slightly higher than that suggested in previous studies. In the previous study, researchers suggested that G value ranges between 180 and 400 rpm for kaolin system [22–26]. However, here we observed that G value range giving the maximum floc formation was between 500 and 600 rpm for picophytoplankton system. For kaolin system, the maximum floc formation was achieved at G value range between 800 and $1,000\text{ rpm}$. Therefore, in contrast to previous studies, the relatively high velocity gradients can be suggested for coagulation process in drinking water treatment.

The maximum size of the flocs was produced with kaolin system in these experiments. In addition, the results demonstrated that the floc formation depended not only on G value but also on the type of coagulant. PSI produced the largest floc with d_{50} size of $351.3\text{ }\mu\text{m}$ at 470 s^{-1} in kaolin suspension, while PACl produced the largest flocs with d_{50} of $287.5\text{ }\mu\text{m}$ at 200 s^{-1} in kaolin suspension. PSI also produced the largest floc in *Synechococcus* sp. suspension. The maximum size of

Synechococcus sp. flocs reached to $238.8\ \mu\text{m}$ at $250\ \text{s}^{-1}$. However, PACl produced the largest *Synechococcus* sp. flocs with d_{50} of $159.2\ \mu\text{m}$ at $200\ \text{s}^{-1}$.

Kan et al. [21] suggested that the rise in residual turbidity in coagulation when the time of rapid mixing increased was caused by the breakage of flocs. Actually, although long rapid mixing time increases the number of collision between flocs, the nature of the floc surface is changed by the repeated breakage and reconnection of floc fragments [5,27,28], which causes lower collision efficiency. Therefore, after longer rapid mixing times, the large floc size decreases and the small floc size increases. Thus, the size of re-growth flocs is smaller than that before breakage and the re-growth flocs are of nearly the same size. In this study, it was noted that the volume of formed *Synechococcus* sp. and kaolin flocs first increased and then decreased with the increased rapid mixing time. The *Synechococcus* sp. floc volume was maximized at the rapid mixing time of 60 and 90s with PACl and PSI, respectively, where the formed floc size mostly distributed in the range between 100 and $1,000\ \mu\text{m}$. This floc size distribution range for kaolin suspension was observed at the mixing time of 60s with both PSI and PACl. From these result, it can be suggested that the rapid mixing time of between 60 and 90s is suitable for raw water treatment.

5. Mechanism

The formation, breakage, and re-growth of picophytoplankton and kaolin flocs were realized in the experiments to investigate the efficiency of different particles systems removal. During the breakage process, the newly exposed surfaces of aggregates may have a net negative, positive, or neutral charge and this may depend on the nature of particles systems. Fig. 8 illustrated the mechanism of flocs formation, breakage, and re-growth. When the coagulant added to system, some of the particles in the system absorb Al^{+3} or Fe^{+3} ions or their variation unevenly; at this instant, the charge neutralization is effective mechanism in coagulation process. The number of collision between flocs increases with increasing velocity gradient and the neutralized particles begin flocs formation. However, when the velocity gradient and rapid mixing time increase much, it caused the breakage of larger flocs. As a result of the breakage of larger flocs, small flocs occur with change in the nature of surface. Some of these small flocs have an “active point (positive or negative charge)” on their surface. These flocs with active points are more prone to form larger flocs. And, if rapid mixing continuous, these active points can keep active points of other small flocs and can form larger flocs. Therefore, the number of active points determines the grown ability of flocs. Here, the charge neutralization is an effective mechanism in

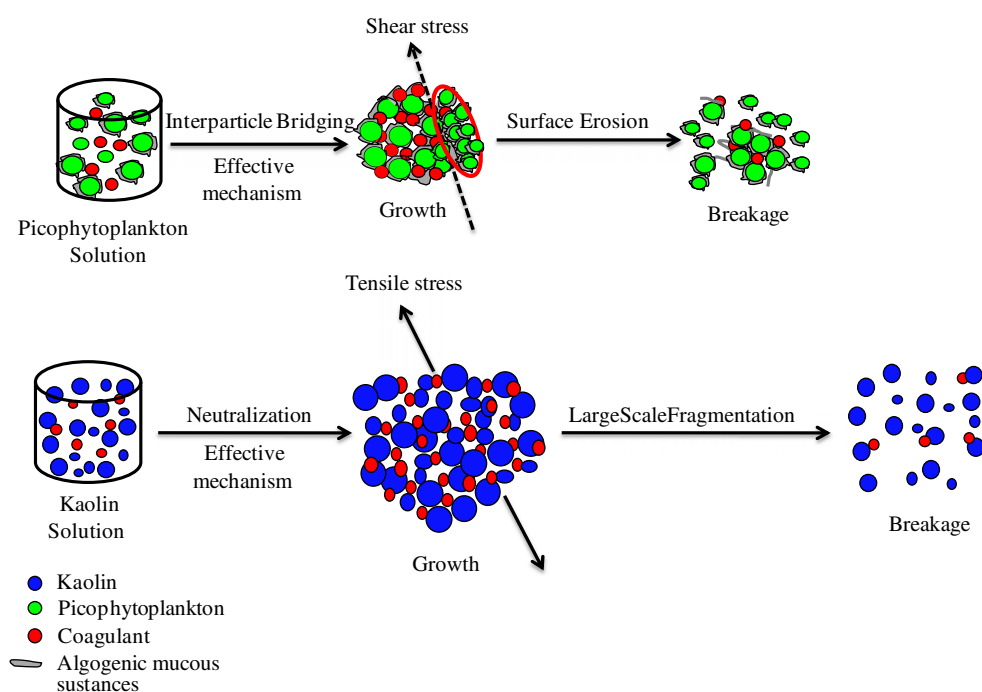


Fig. 8. The mechanism of flocs formation and breakage.

coagulation process. There are also some neutral-charged small flocs in the system. These flocs also can form larger flocs by sweeping mechanism. However, the flocs were formed by sweeping mechanism with loose and branchy in comparison to flocs formed by charge neutralization mechanism [29,30]. The results showed that the re-growth rate of *Synechococcus* sp. system was larger than that of kaolin system. It may be attributed that *Synechococcus* sp. flocs have more “active point” due to their variable surface properties in comparison to kaolin. This infers that the effect of velocity gradient and rapid mixing time is significantly different.

6. Conclusions

This is the first study to determinate the effects of velocity gradient and rapid mixing time on the picophytoplankton removal in drinking water treatment. For this purpose, the effect of G value and rapid mixing time was investigated. Several jar tests were performed in the various combinations of G value and mixing time, and the main conclusions are as follows:

- (1) Three different zones were found to be depending on G value in coagulation process. At low G value, the aggregation dominated over breakup. At mean G values, flocs formation was maximized, producing the largest flocs. For large G values, breakup dominated over floc formation. In the last case, an increase in the shear rate caused a reduction in the mean particle size (d_{50}).
- (2) Longer rapid mixing speed caused decrease in the volume of formed flocs. Although the rapid mixing time influenced the coagulation efficiency, the size of the re-growth flocs after breakage was nearly the same. The rapid mixing time between 60 and 90 s may be applied to both *Synechococcus* sp. and kaolin system.
- (3) Kaolin flocs had relatively high ability to withstand shear in the jar tester compare to *Synechococcus* sp. flocs. However, *Synechococcus* sp. flocs had relatively high re-growth ability than kaolin flocs after the breakage period.
- (4) The re-growth of flocs was controlled not only by G value or the rapid mixing time but also by the characteristics of different coagulants.
- (5) G value range giving the maximum floc formation was between 500 and 600 rpm for picophytoplankton system. For kaolin system, the maximum floc formation was achieved at G value range between 800 and 1,000 rpm. Therefore, in contrast to previous studies, the relatively high velocity gradients can be suggested for coagulation process in drinking water treatment.

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