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Comparison of four kinds of coagulants for the removal of picophytoplankton

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ABSTRACT

The purpose of this study was to investigate the efficiency of the coagulation process for the removal of picophytoplankton from drinking water and, in addition, to investigate the performance of simple coagulants such as alum and ferric chloride, and polymer coagulants such as PAC and PSI, in picophytoplankton removal. Two simple coagulants such as alum ($Al_2(SO_4)_3{\cdot}16H_2O$) and ferric chloride ($FeCl_3{\cdot}6H_2O$) and two polymer coagulants such as poly-silicate iron (PSI) and poly-aluminum chloride (PAC) were used in both raw water including picophytoplankton and synthetic water samples prepared by *Synechococcus* sp. Analyses included a picophytoplankton count, an assessment of the turbidity, dissolved organic carbon, UV_{254}, and zeta potential and the settling time measurements. The removal efficiency of picophytoplankton during the coagulation–flocculation–sedimentation process was determined using simple and polymer coagulants. Water samples with lower coagulation pH had better picophytoplankton removal in coagulation–flocculation–sedimentation. The results indicate that even low coagulant doses of PSI in both raw water and artificial water performs better than the other three types of coagulants in terms of picophytoplankton, turbidity, UV_{254}, and DOC removal.

Keywords: Picophytoplankton; Polymer coagulant; Coagulation; Sedimentation; Zeta potential; Drinking water treatment

1. Introduction

Picophytoplankton (picoplanktonic cyanobacteria) is a small plankton ranging between 0.2 and 2 μm in size, comprised of picocyanobacteria and eukaryotic phototrophs. They are distributed worldwide and are ubiquitous in all type of ponds, lakes, and ocean, and of varying trophic states [1]. Since the picophytoplankton has a great importance in the food web chain in aquatic ecosystem, therefore, they have been intensively studied.

Picophytoplankton is an important consideration not only in terms of the ecosystems but also with regard to drinking water treatment. 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

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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, the formation of assimilable organic carbon (AOC), disinfection byproducts (DBPs), and various other toxins [2,3]. The influence of picophytoplankton and their intracellular metabolites on water quality and human health was first reported in the 1980s. Faust and Aly [4] reported that picophytoplankton affected the water color and gave it a musty or fishy odor. Nakamura et al. [5] and Hoson et al. [6] showed that picoplankton, especially picophytoplankton, contributed to the turbidity of treated water. In addition, Domingos et al. [7] reported that picoplanktonic cyanobacteria contribute to microcystin production and picoplanktonic cyanobacteria species behaves much like other microcystin-producing cyanobacterial species with regard to poison. Carmichael et al. [8] reported that picophytoplankton *Synechococcus* produces microcystin which can cause liver disease in human beings.

The above-mentioned toxic compounds of picophytoplankton are released into the surrounding water when cells die or cell lysed by a disinfection process, which poses an additional problem in drinking water treatment plants. Therefore, the best strategy is to remove picophytoplankton without damaging the cell integrity through a coagulation process. Despite the many negative effects of picophytoplankton, the removal of picophytoplankton from drinking water has not been well studied. Some have suggested that this is due to the difficulty of observing and identifying these extremely small sized of micro-organisms [7,9]. The few studies conducted on the treatment of picophytoplankton have found that it is difficult to remove picophytoplankton in the conventional drinking water treatment process, i.e. by using coagulation–sedimentation and filtration. Okuda et al. [10] reported that the removal percentage of picophytoplankton ranges (initial concentration: 1.1×10^4–1.2×10^4 cells/mL) from 44% to 60% with an optimum coagulant dose of PAC in the coagulation–sedimentation process. Rapenne et al. [11] showed that almost 62% of picophytoplankton (initial concentration: 1.0×10^4 cells/mL) removed with 4 mg/L coagulant dose in coagulation–sedimentation and an 8 h filtration process. In another study, it was shown that *Synechococcus* is the most difficult removing species among Picoeukaryotes, *Prochlorococcus,* and *Synechococcus* to remove by conventional water treatment systems.

The effectiveness of picophytoplankton removal through coagulation is strongly determined by the type of coagulant. Aluminum and iron salts are widely used for coagulation in drinking water treatment. However, despite their similarities, the affinity of each coagulant for different impurities is known to vary [12–15]. Some researchers reported that both coagulant species have different effect on bacteria removal due to their varying cellular characteristics such as their size, surface chemistry, surface charge, and the density of the cell [16]. For example, Jiang and Graham [17] reported that aluminum-based coagulant removed Anabaena flos-aquae (initial concentration: 2×10^5 cells/mL) by 78% at 5.4 mg/L of Al salts. However, an iron-based coagulant under the same experiment conditions removed 74% of Anabaena flos-aquae (initial concentration: 2×10^5 cells/mL) at a concentration of 11.2 mg/L of iron salts. In other studies, a 5 mg/L solution of $Fe_2(SO_4)_3$ was shown to remove 62% of Microcystis aeruginosa (initial concentration: 5.8×10^4 cells/mL) and a 5 mg/L poly-ferric sulfate solution (PFS) was found to remove 81.6% of Microcystis aeruginosa (initial concentration: 5.8×10^4 cells/mL) [18]. Okuda et al. [19] reported that the performance of PSI for synthetic *Cryptosporidium* oocyst removal was higher than PAC and ferric chloride. Although there are numerous studies about the removal of cyanobacteria, the coagulation of picophytoplankton using a coagulation–flocculation technique with different aluminum- and iron-based coagulants has not yet to be reported.

The purpose of this study was to investigate the efficiency of the coagulation process for the removal of picophytoplankton from drinking water and, in addition, to investigate the performance of simple coagulants such as alum and ferric chloride, and polymer coagulants such as PAC and PSI, in picophytoplankton removal. Raw water including picophytoplankton and the artificial water samples were used in this study.

2. Materials and methods

2.1. Raw water

The raw water samples were taken from the Kunimi Water Treatment Plant (KWTP) in Sendai. KWTP is supplied by Okura Dam reservoir in the northwest of Sendai. The volume of the reservoir is approximately 28,000,000 m^3. The properties of the raw water are summarized in Table 1. The raw waters samples were collected prior to any pretreatment from the inlet channel of the KWTP and were transported to the laboratory on the same day. The raw water samples were kept in the refrigerator at +4 °C until all the experiments were completed.

2.2. Picophytoplankton culture

The cyanobacterium *Synechococcus* sp. strain (NIES-1348) was obtained from the National Institute for

Table 1
Okura Dam water quality parameters

Variables (unit)	Range	Averages
Turbidity (NTU)	2.4–5.3	4.2
DOC (mg/L)	2.45–4.15	3.14
UV_{254} (1/cm)	0.085–0.165	0.151
Alkalinity (mg $CaCO_3$/L)	11.4–44.0	23.5
Picophytoplankton (cells/mL)	118–5157	3536

Environmental Studies (NIES) in Japan and cultivated in an axenic CB medium at 25 ± 1°C under fluorescent light (18 μmol photons/m^2/s, 12-h light/12-h dark). About 100 mL of each of the CB medium was composed of 15 mg C $Ca(NO_3)_2{\cdot}4H_2O$, 10 mg KNO_3, 5 mg β-Na_2 glycerophosphate. $5H_2O$, 4 mg $MgSO_4{\cdot}7H_2O$, 0.01 μg Vitamin B_{12}, 0.01 μg Biotin, 1 μg Thiamine HCl, 50 mg Tris (hydroxymethyl) aminomethane, 0.3 mg/L $Na_2EDTA{\cdot}2H_2O$, 0.0588 mg/L $FeCl_3{\cdot}6H_2O$, 0.0108 mg/L $MnCl_2{\cdot}4H_2O$, 0.0031 mg/L $ZnSO_4{\cdot}7H_2O$, 0.0012 mg/L $CoCl_2 \cdot 6H_2O$, and 0.00075 mg/L $Na_2MoO_4{\cdot}2H_2O$. The pH of the medium was adjusted by adding either 0.1 M NaOH or 0.1 M HCl. *Synechococcus* were grown in a 200 mL of Erlenmeyer flaks 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 at a light microscope. The cells in the stationary phase of the culture where the population density was at its highest (Fig. 1) were used for the experiments.

2.3. Artificial water

The artificial water experiments were performed with tap water, including 0.35 mM $NaHCO_3$ and 1.5 mM NaCl. A cell suspension of about 50,000,000 cells/mL was obtained after cultivation. It was diluted by a factor of 50 with deionized water for use in the experiments. The artificial water had the following characteristics: a pH of 7.3–7.6, a turbidity of 5.35 ± 2.5 NTU, and an approximate cell concentration of 1×10^6 cell/mL.

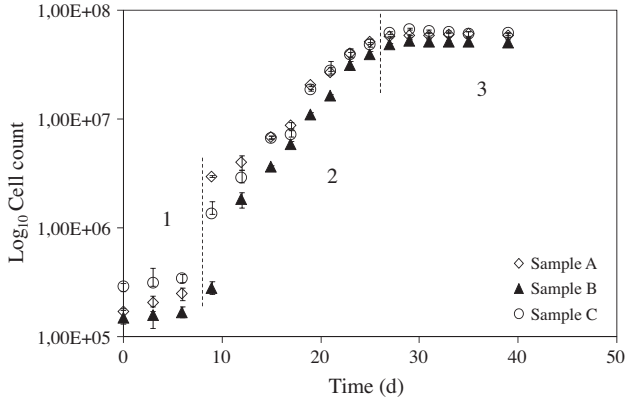

Fig. 1. The growth phases of *Synechococcus* in three cultivating flasks 1. Lag phase; 2. Growth phase; and 3. Stationary phase.

2.4. Analytical methods

The turbidity of the samples was measured using a Water Anlyzer WA600 turbidity meter (Nippon Denshoku Industries, Japan). A Shimadzu 500A TOC analyzer was used to determine the DOC content. UV-Abs (1/cm) at a wavelength of 254 nm was measured with a 1 cm quartz cell using a Shimadzu UV-1700 PharmaSpec UV–VIS spectrophotometer. All the samples were passed through a Millipore Inc. cellulose acetate syringe filter before both UV and DOC analyses. The coagulation and flocculation experiments were carried out in a six-paddle jar tester. The picophytoplankton cells in the treated water samples were counted with AxioCam HRc camera microscope (Zeiss, USA). The zeta potential measurements of samples were obtained using a Micro-Electrophoresis Apparatus Mk II (Rank Brothers, UK). The zeta potential was evaluated at a room temperature of 20 ± 1°C and a suspension under an applied electric field of 80 mV. The zeta potential was calculated from the measured mobility according to the Smoluchowski equation. The pH was adjusted to a pH range of 5–10 using of HCl and NaOH. Furthermore, the zeta potential of coagulated samples was measured as a function of the coagulant dosage after the coagulation experiments. All the figures in this study were plotted using Microsoft Excell 2003.

2.5. Reagents

The reagents including ferric chloride ($FeCl_3{\cdot}6H_2O$), alum ($Al_2(SO_4)_3{\cdot}16H_2O$), and PAC were obtained from Kanta Chemical Co. Inc., and PSI (28.7% as SiO_2 and 33% as Fe) was obtained from Suido Kiko Kaisha Ltd. (Tokyo, Japan). Stock solutions of all reagents were prepared in distilled water.

2.6. Jar test experiments

Jar testes were performed using both the raw water and the artificial water including picophytoplankton at room temperature (about 20 ± 1°C), by a six-paddle stirrer. The cell number was counted in both water samples, before the jar test. The beakers were then placed on the jar test apparatus and while they were being rapidly mixed for 3 min at 150 rpm, various doses of ferric chloride, alum, PAC, and PSI

from 10 to 100 mg/L were added to the water. After this mixing, the zeta potential of the samples was measured and the samples were slowly mixed for 30 min at 30 rpm, before being settled for a period of 60 min. At the end of the settling period, the supernatant was taken at 3 cm below of the water surface level using a pipette to determine the residual cell concentration, the turbidity, DOC, and the UV_{254}. The pH of surface water and picophytoplankton suspension was adjusted 5.0–8.0 with 1 M HCL or 1 M NaOH when dosing the coagulants.

3. Results and discussion

3.1. Number of picophytoplankton in raw water

The raw water was sampled from KWTP through the experiments. Fig. 2 shows the change of picophytoplankton density in raw water.

Picophytoplanktons are present at all the sampling times, albeit at low population densities, with cell counts recorded between 118 and 5157 cells/mL in 2009 and 2010. Peaks in cell counts were observed in May 2010.

Fig. 3 shows the relationship between turbidity and the picophytoplankton cell count in the raw water. A linearly proportional relationship between the raw water turbidity and picophytoplankton cell number was observed for each sampling. It is concluded that picophytoplankton contributes to the turbidity of the raw water.

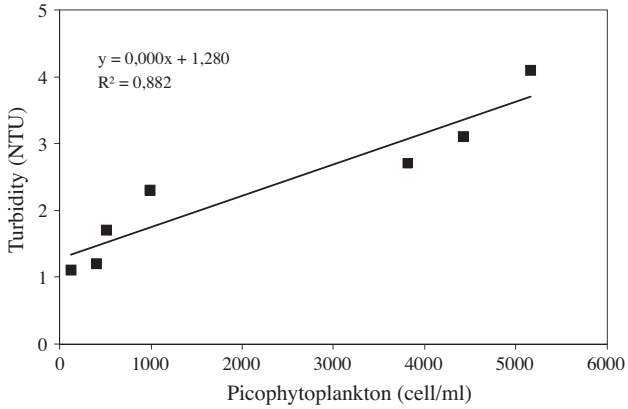

Fig. 3. Relationship between turbidity and picophytoplankton cell count in raw water.

3.2. Effect of coagulant type

3.2.1. Raw water experiments

Despite their similarities, however, the affinity of each coagulant for different impurities is known to vary. Therefore, we examined the effect of different types of coagulants in the water treatment. Fig. 4 shows the effect of the coagulant dose on the removal of turbidity by coagulation–sedimentation using the four coagulants. The turbidity removals were shown to vary with the different coagulants at the same dose. For example, 60 mg/L of coagulant gave maximum turbidity removal for PSI and PAC. The turbidity removal rates, however, were also shown to differ. This is likely due to the important role polymer bridging plays in turbidity removal. Polymer bridging is facilitated by higher molecular weight polymers with a relatively low charge density. PSI had a higher molecular weight (m.w. = 500,000 dalton) than PAC (m.w. = 440,000 dalton) and the other two coagulants; therefore, PSI showed large turbidity removal rate compare to the other coagulants [19].

It was found that the turbidity removal was 90.4% for PSI and 83.3% for PAC at a coagulant dose of 60 mg/L. At doses of over 60 mg/L of PSI and PAC

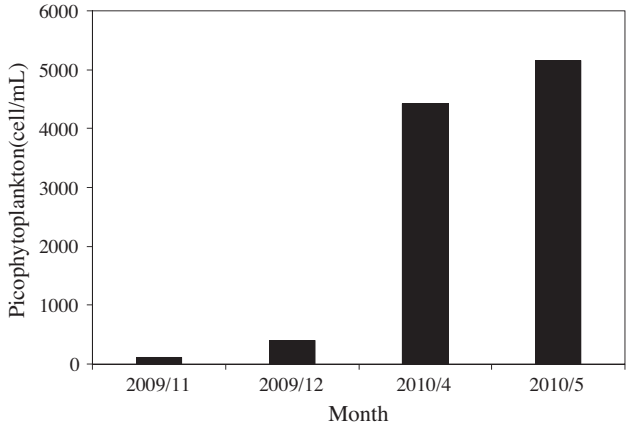

Fig. 2. Change of picophytoplankton cell density in raw water.

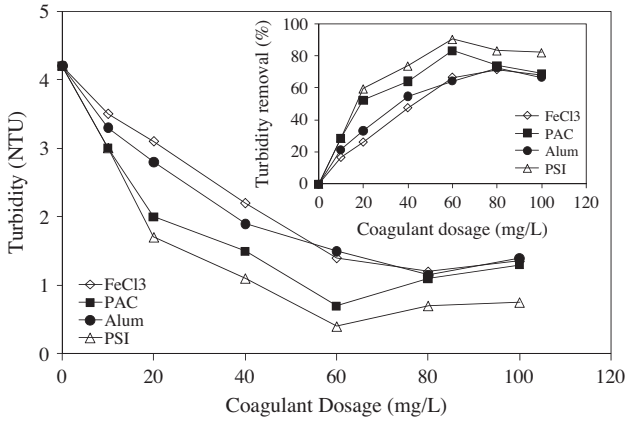

Fig. 4. Turbidity removals with each type of coagulant in raw water (initial turbidity: 4.2 NTU).

the turbidity removal rate slightly decreased. This can be attributed to the restabilization of particles due to the formation of positively charged small flocs, and particularly the formation of high-charged polymer species [20]. Compared to PAC and PSI, a larger coagulant dose of alum and ferric chloride were required for the maximum turbidity removal. It was observed that a dose of 80 mg/L of alum and ferric chloride resulted in the maximum turbidity removal, achieving 72.6% and 71.4% turbidity removal, respectively. It should be pointed out that the turbidity removal was not only controlled by the coagulant dose but also by the type of coagulant.

Fig. 5 shows the removal rate of picophytoplankton during sedimentation after coagulation with the four coagulants. The picophytoplankton content of the suspension was counted after sedimentation. The results indicated that the picophytoplankton removal of PSI was more effective than the other three coagulant types, as was also the case for the turbidity removal. The high picophytoplankton removal performance of PSI can be attributed to its high reduction rate of small particles during coagulation and also the higher sedimentation rate of flocs. Both of these factors have been attributed to the polymerized silica in PSI [19]. Whilst these bigger flocs precipitate, picophytoplankton cell can be adsorbed onto the surface of flocs or can be embedded in to the flocs before precipitating with formed flocs. Our results indicate that the floc formation followed by sweep coagulation is an effective mechanism for the removal of picophytoplankton. The picophytoplankton concentration in settling water with 60 mg/L dose of PSI reached its lowest value at 46 cells/mL. The residual picophytoplankton cell number slightly increased with the increasing coagulant concentration till 100 mg/L PSI. The slight increase in the residual picophytoplankton number can be attributed the charge reversal with the increasing coagulant dose. A similar trend was observed for both PAC and ferric chloride. Residual picophytoplankton numbers between 399 cells/mL and 539 cells/mL were observed with doses of 60 mg/L PAC and ferric chloride, respectively. The maximum picophytoplankton removal was achieved with a coagulant dose of 80 mg/L for alum: a residual picophytoplankton number of 543 mg/L was observed. These results indicate that more effective treatment was achieved with lower doses of PSI compared to other coagulants. In other words, PSI use allows for the most effective treatment at a reasonable cost. Floc formation and sweep coagulation were shown to be the predominant mechanisms for picophytoplankton removal. In addition, it can be concluded that the removal of picophytoplankton is more difficult than the removal of turbidity.

On the other hand, the data show a log-linear relationship between the residual turbidity and picophytoplankton cells for all four coagulants (Fig. 6). This relationship indicates that most of flocs were complexes of turbid material and picophytoplankton cells. Any remaining turbidity in the water after the coagulation may be due to untreated picophytoplankton cells.

3.2.2. Zeta potential

The charge neutralization of each coagulant is different, depending on the relative valence of the ions, hydrolyzed products, and on their concentration. In this study, therefore, the charge neutralization

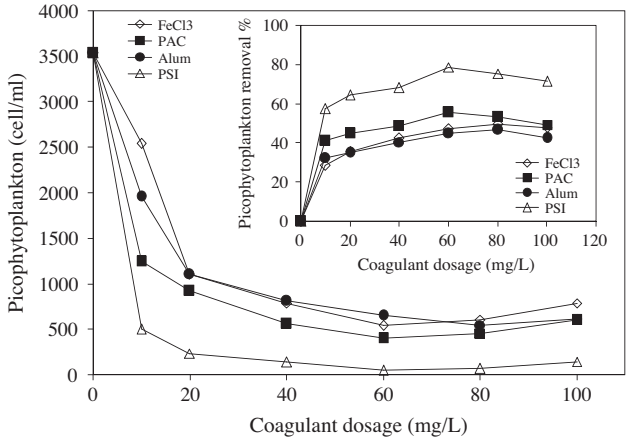

Fig. 5. Picophytoplankton cells removals for each type of coagulant in raw water (initial picophytoplankton: 3536 cell/mL).

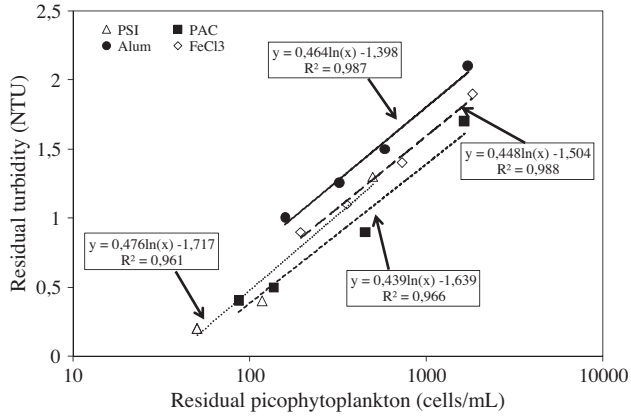

Fig. 6. Relationship between the residual picophytoplankton and turbidity.

capability of different coagulant types was also determined. Fig. 7 illustrates the zeta potential measurements, which can serve as an indicator of the coagulants components impact on the surface charge of colloids and cells. The differences between the coagulants are small, but it is clear that PSI exhibit the biggest impact on the zeta potential of system. Therefore, it can be suggested that the addition of PSI reduces the zeta potential of the raw water samples with picophytoplankton more effectively than PAC and the other simple coagulants.

The highly charged polynuclear iron hydrolysis products of PSI may be the reason for its effectiveness at removing picophytoplankton. With PSI, the zeta potential of the raw water reached the isoelectric point at a coagulant dose of 65 mg/L, whereas with PAC, ferric chloride, and alum, charge reversal occurred at a coagulant dose of 73 mg/L, 73 mg/L, and 86 mg/L, respectively. The weakest effect on the zeta potential of raw water was exhibited by alum. The charge neutralization ability of the coagulants used in this study may be showed as followed an increasing order: alum < ferric chloride = PAC < PSI.

3.2.3. DOC and UV_{254} removal

The effect of coagulant type on DOC and UV_{254} removal was monitored for all samples. The most efficient coagulant both for DOC and UV_{254} removal in raw water was PSI, as shown in Fig. 8. This can be explained by the high neutralization ability of the PSI coagulant: when the polymerized silica and iron combine the adsorption, bridging, and neutralization properties of PSI improve, in effect improving the DOC and UV_{254} removal rate [19,21]. Another factor may be the better DOC adsorption capacity of PSI [21].

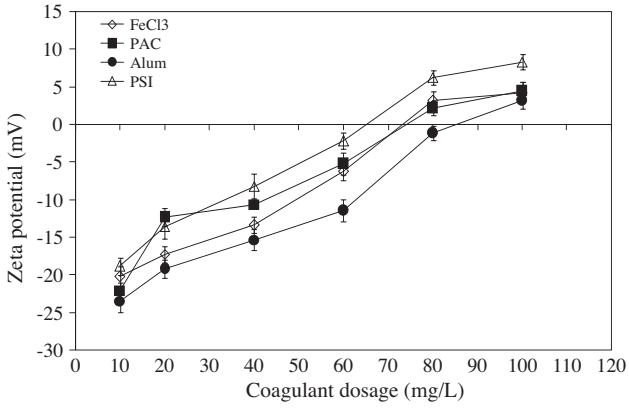

Fig. 7. The effect of coagulant type on Zeta potential.

The maximum DOC and UV_{254} removal amount was achieved at 100 mg/L PSI. At this dosage, the percent removal of DOC and UV_{254} were 71% and 82%, respectively. With all four coagulants, DOC and UV_{254} removal gradually increased with an increasing coagulant dose. Maximum DOC and UV_{254} removal were achieved with PAC, ferric chloride and alum at a dose of 100 mg/L. The maximum DOC and UV_{254} removal was 48% and 70% for ferric chloride, 42% and 66% for PAC and 33% and 51% for alum, respectively. At the maximum coagulant dose of 100 mg/L, the iron-based coagulants PSI and ferric chloride, showed greater removal efficiency than that the aluminum-base coagulants PAC and alum. This can be attributed to the higher molecular weight of the iron-based coagulants which gives them a higher precipitation capacity. Our results indicate that the iron-based coagulants enhance the removal of DOC and UV_{254}.

3.2.4. Artificial water

Jar test experiments in artificial water were carried out in artificial water to better understand the direct

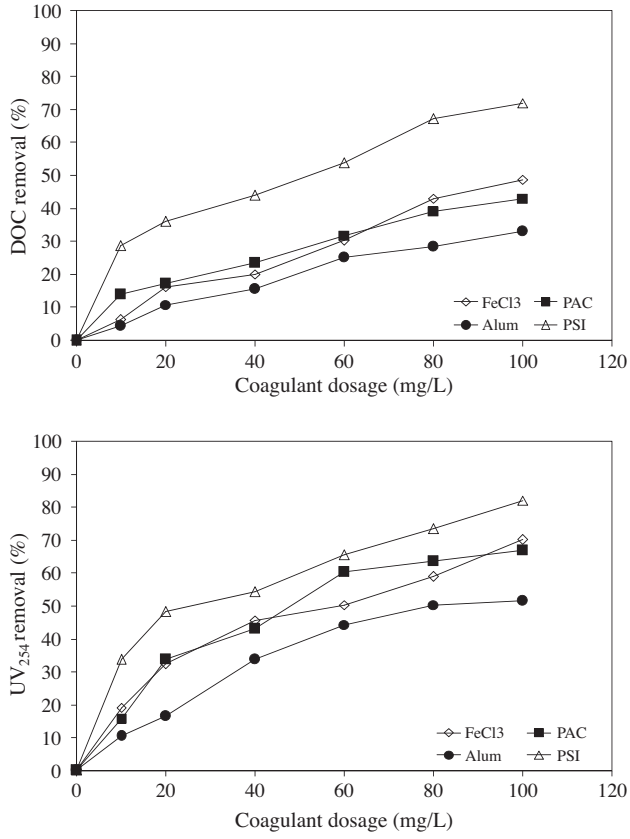

Fig. 8. The effect of coagulant type on removal of DOC and UV_{254} (initial DOC: 3.14 mg/L, UV_{254}: 0.151 1/cm).

interaction between picophytoplankton cells and the coagulants. For the purpose of these experiments, *Synechococcus* sp. was cultivated in the laboratory and added to 1 L of deionized water with a predetermined concentration of *Synechococcus* sp. cells. Fig. 9 shows picophytoplankton removal in the artificial water by the coagulation and sedimentation process using the four coagulants. As was the case with the raw water experiments, the highest *Synechococcus* sp. removal was obtained with PSI. Nevertheless, the *Synechococcus* sp. removal rate was considerably lower and the coagulant demand was considerably higher in comparison to the raw water.

The low *Synechococcus* sp. removal rate may well be due to the low size and density of the formed floc. Although the zeta potential of *Synechococcus* sp. was neutralized with a large dose of the coagulant, a negligible quantity of floc was formed. The density of the formed floc may have been closer to the density of the water, resulting in a sharp reduction in the amount of *Synechococcus* sp. floc sediment.

Since a coagulant dose of 100 mg/L was not sufficient to neutralize the zeta potential of *Synechococcus* sp. during the coagulation, the dosage was increased to 500 mg/L in the artificial water experiments. The high coagulant demand of *Synechococcus* sp. may be due to the chelate complex formation between the extracellular organic matter/cellular organic matter of *Synechococcus* sp. and the coagulants. Takaara et al. [22] showed the effects of algogenic organic matter in coagulation which in turn produce a coagulant demand. Auvray et al. [23] found emphasized that both extracellular and organic matter (EOM) and cellular organic matter (COM) disturb the flocculation of suspended kaolin with PAC, and suggested that the proteins in COM inhibit coagulation by consuming the coagulant on the coagulation process due to the formation of chelate complexes between these inhibitory proteins and the coagulant. In this study, therefore, the consumption of coagulants by *Synechococcus* sp. proteins may have been one of the main factors of the increase in coagulant demand. Maximum *Synechococcus* sp. removal was achieved as 36%, 31%, 26%, and 24% for PSI, PAC, ferric chloride, and alum, respectively. As shown in Fig. 10, with higher doses of all four coagulants the zeta potential gradually became positive. The results showed that less PSI was necessary to neutralize the zeta potential of *Synechococcus* sp. than other coagulants. A coagulant dose of approximately 120 mg/L was required to reach the isoelectric point of *Synechococcus* sp. whereas it was approximately 260 mg/L for PAC, 280 mg/L for ferric chloride, and 380 mg/L for alum. The neutralization efficiency of each coagulant is differs considerably. The zeta potential values at maximum picophytoplankton cell removal were measured as +16.58 mV, +12.58 mV, +9.89 mV, and +5.1 mV for PSI, PAC, ferric chloride, and alum, respectively. These results clearly show that a larger coagulant dose is required to neutralize the zeta potential of picophytoplankton in turbid materials than in raw water.

3.3. Effect of pH on coagulation

3.3.1. Raw water

Solution pH during coagulation affects the chemistry of the coagulant. When the coagulants added to water, the different hydrolysis products are formed, including monomers, oligomers, and polymeric hydroxyl complexes under different pH conditions. Therefore, the effect of pH on the coagulation behavior of

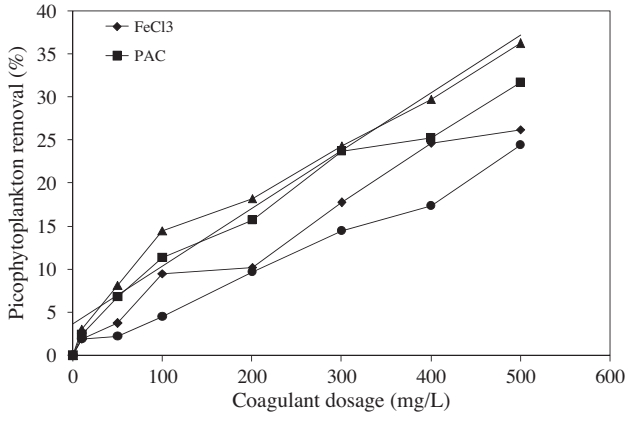

Fig. 9. Picophytoplankton cells removals for each type of coagulant in artificial water (initial picophytoplankton: 2×10^6 cell/mL).

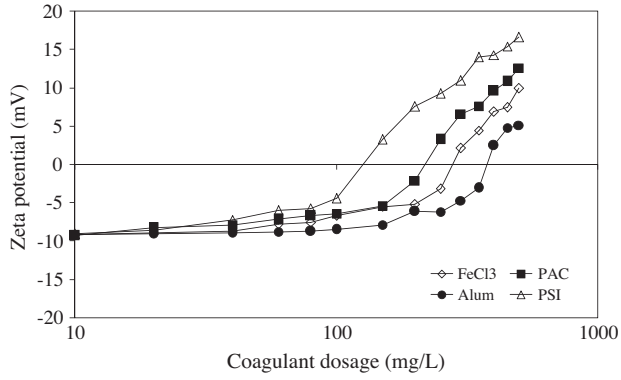

Fig. 10. Zeta potential of picophytoplankton cell in synthetic water.

aluminum- and iron-based coagulants was examined in the range of pH 5.0 and 8.0 at a coagulant dose of 60 mg/L. These results of the picophytoplankton and turbidity removal are shown in Figs. 11 and 12, respectively.

As shown in Fig. 11, PSI at various pH conditions showed better coagulation efficiency than other coagulants. For each type of coagulant the residual picophytoplankton decreased sharply when the pH decreased from 8.0 to 6.5, and then slowly increased from pH 6.5 to 5.0, with the exception of ferric chloride. However, all four coagulants showed better efficiency in the slightly acid conditions than in the basic conditions. The removal rate of the polymer coagulants, PSI and PAC was higher in the range of pH 5.0–8.0 than the more simple coagulants, ferric chloride and alum. The maximum picophytoplankton removal rate was obtained at pH 6.5, with rates of 96% and 90% for PSI and PAC, respectively, whereas it was at pH 6.0, with rates of 87% and 85% for ferric chloride and alum. The optimum pH range for picophytoplankton removal was between pH 6.0 and 6.5 for PSI, PAC, and alum and pH 5.5–6.5 for ferric chloride. The wider applicable pH range observed for ferric chloride than for the other three coagulants can be explained by its lower hydroxylation and polymerization rates [24]. This pH range corresponds to the pH range which is suggested by US Environmental Protection Agency (EPA) for drinking water [25].

Fig. 12 shows the effect of coagulation pH on residual turbidity in raw water. Turbidity is reduced most effectively with all four coagulants in slightly acidic pH regions. The higher bridging ability of PSI provided better turbidity removal. The maximum turbidity removal was achieved at around pH 6.5 for PSI, PAC, and alum, and at around pH 6.0 for ferric chloride. With a pH below 6.5, the turbidity removal efficiency of PAC and alum significantly decreased whereas only a slightly decrease was noted for PSI. The decrease of turbidity removal seems to be the result of particle restabilization which occurs at pH 6.0 for PSI, PAC, and alum. It may be that the high content of polymer species leads to the formation of positively charged small flocs [24]. The optimum pH range for efficient turbidity removal appears to be between pH 5.5 and 6.5 for PSI and ferric chloride and at a pH of 6.5 for PAC and alum. The maximum turbidity removal was achieved at pH 6.5 with 91%, 83%, and 79 % removal for PSI, PAC, and alum, respectively. It should be noted, however, that the maximum removal for ferric chloride was 85% at a pH of 6.0. The results indicate that PSI showed better coagulation performance for both picophytoplankton and turbidity removal than the other coagulants.

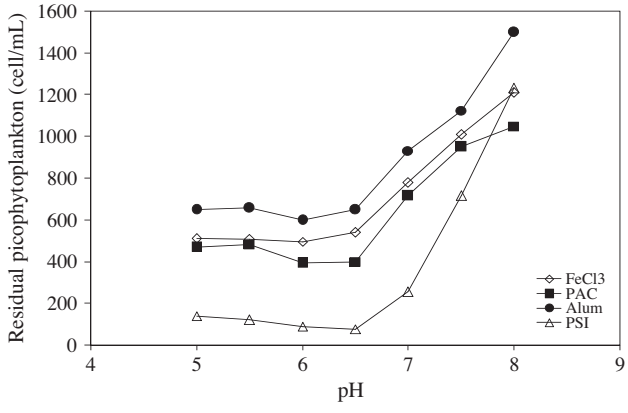

Fig. 11. Effect of pH on picophytoplankton removal (initial picophytoplankton: 4128 cells/mL; coagulant dose: 60 mg/L).

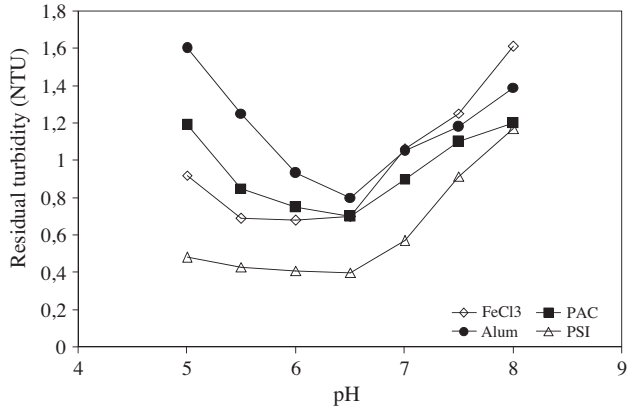

Fig. 12. Residual turbidity at each coagulation pH (initial turbidity: 4.2 NTU; coagulant dosage: 60 mg/L).

3.3.2. *Artificial water*

The influence of coagulation pH on artificial water including *Synechococcus* sp. was tested using each coagulant type within a pH range of pH 5.0–8.0. Fig. 13 shows the residual *Synechococcus* sp. cell in the artificial water. Fig. 13 indicates that *Synechococcus* sp. removal at a lower pH is slightly better than at basic pH values.

Synechococcus sp. removal slightly increased when the coagulation pH decreased from 8.0 to 5.0. However, this had a negligible effect on the total *Synechococcus* sp. removal. Because the formed flocs were too small and their density was too low to precipitate, a high amount of picophytoplankton remained in the artificial water. The maximum picophytoplankton removals were at a pH 5.5 for PSI

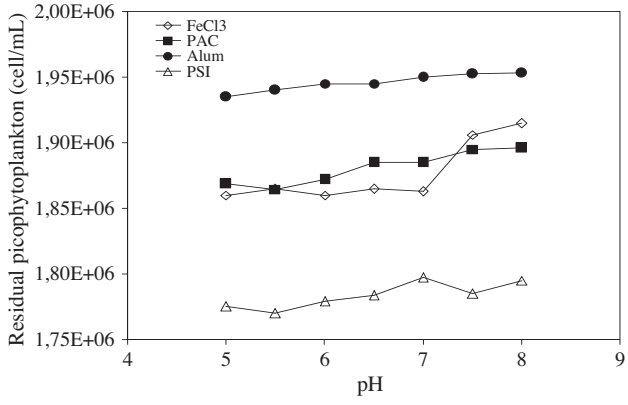

Fig. 13. Residual picophytolankton at each coagulant pH (initial picophytoplankton: 2×10^6 cell/mL).

and alum with 11.5% and 3% removal, respectively, and 6.4% removal at pH 6.0 for PAC and ferric chloride. The latter are considered too low for drinking water treatment facilities.

3.4. Sedimentation characteristic

The sedimentation characteristics of the picophytoplankton and turbid materials were evaluated in order to elucidate the differences in the removal performance between the polymer (PSI and PAC) and simple coagulants (ferric chloride and alum). The sedimentation performance of floc produced was evaluated on the basis of settling time. The results showed that there was no significant difference in the final concentration of the residual picophytoplankton cell number for 180 min for PSI, PAC, and ferric chloride. However, the difference between PSI and the other three coagulants in the residual number of picophytoplankton at the initial stage (up to 30 min), was substantial, indicating the presence of a larger number of either big or high-density flocs, which quickly settled within 30 min. The maximum picophytoplankton removal was achieved with PSI. It is observed that the dimensions of the flocs formed by PSI were relatively larger than those formed by PAC, ferric chloride, and alum, and that this may have had a positive effect on picophytoplankton removal. This observation has been supported by the previous authors who noted coagulation with PSI produced bigger flocs than with PAC, and alum and effective bacteria removal because of the bound polymerized silica of PSI and effective for bacteria removal [26,27]. Furthermore, since the average molecular weight of PSI is higher than the other coagulants, the increment of the density of picophytoplankton floc can also be expected to be higher in PSI experiments, and result in higher sedimentation performance. This difference brought about the difference in picophytoplankton removal. It can be concluded then that the use of PSI is the enhanced coagulation of picophytoplankton and turbidity removal. This is supported by the data in Fig. 14, with the number of residual picophytoplankton for PSI, PAC, ferric chloride, and alum were at 411, 501, 629, and 1020 cell/mL at 180 min of sedimentation, respectively.

The residual turbidity rate at various settling times during the raw water experiments is shown in Fig. 15. The turbidity removal trend was almost the same as picophytoplankton removal. Again, PSI was more efficient in turbidity removal than the other three coagulants by means of settling performance. The residual turbidities at 180 min of sedimentation were 0.15, 0.25, 0.42, and 0.84 NTU for PSI, PAC, ferric chloride, and alum, respectively. The effect of sedimentation time on picophytoplankton removal in the artificial water with the four coagulants was also investigated.

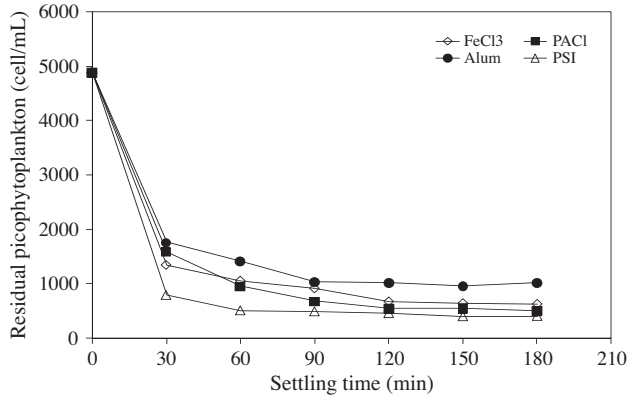

Fig. 14. Residual picophytoplankton at various settling times (initial picophytoplankton: 4890 cell/mL).

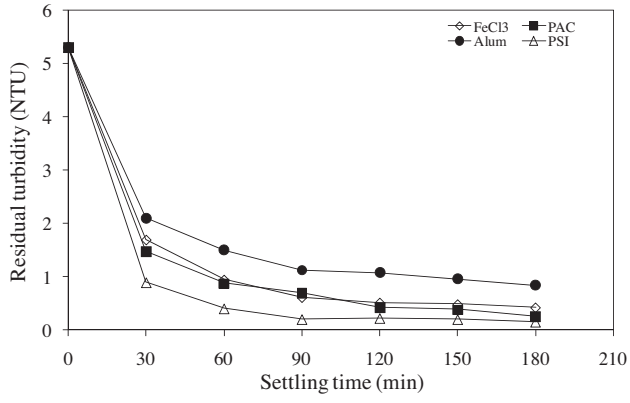

Fig. 15. Residual turbidity with various settling times (initial turbidity: 5.3 NTU).

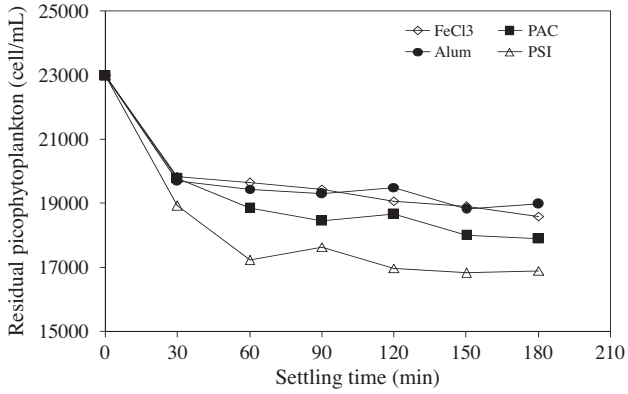

Fig. 16. Residual picophytoplankton at various settling times (initial picophytoplankton: 23,000 cell/mL).

Fig. 16 shows the number of residual picophytoplankton in the artificial water at various settling times. Even though PSI showed the best performance, the picophtoplankton removal in the artificial water was limited. The underlying reason may be that the flocs were very small and did not form a sediment during the settling time. Therefore, it was concluded that the picophytoplankton removal depends significantly on floc formation with turbid materials in the system since the small picophytoplankton flocs need to be absorbed on the surface of big and heavier flocs or become entrapped in the inner part of a larger floc for sedimentation.

4. Conclusions

The purpose of this study was to investigate the picophytoplankton removal efficiency and the mechanism of the coagulation process, as well as the performance of different types of coagulant on the coagulation process. The specific conclusions of this study are as follows:

- PSI showed that the best performance both in raw water and artificial water experiments in terms of the picophytoplankton, turbidity, UV_{254}, and DOC removal among all four coagulants and required a lower coagulant dose.
- The removal of picophytoplankton and turbidity in the coagulation process proceeded best at lower pH levels.
- Both the charge neutralization and sweep coagulation were effective mechanisms for picophytoplankton removal in raw water experiments.
- The artificial water experiments showed that sedimentation performance of picophytoplankton was significantly dependent on floc formation with turbid materials in the system.
- Since polymer coagulants performed better than conventional coagulants in all the coagulation experiments, polymer coagulants can be used to enhance coagulation.

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