TOHOKU UNIVERSITY
Graduate School of Engineering
Ecological Engineering Laboratory

Study on Effect of Particle Size on Coagulation and Advanced Treatment of Fine Particles

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Ph.D. Thesis

Introduction

Fine particles such as picophytoplankton and microplastics abundant in freshwater.

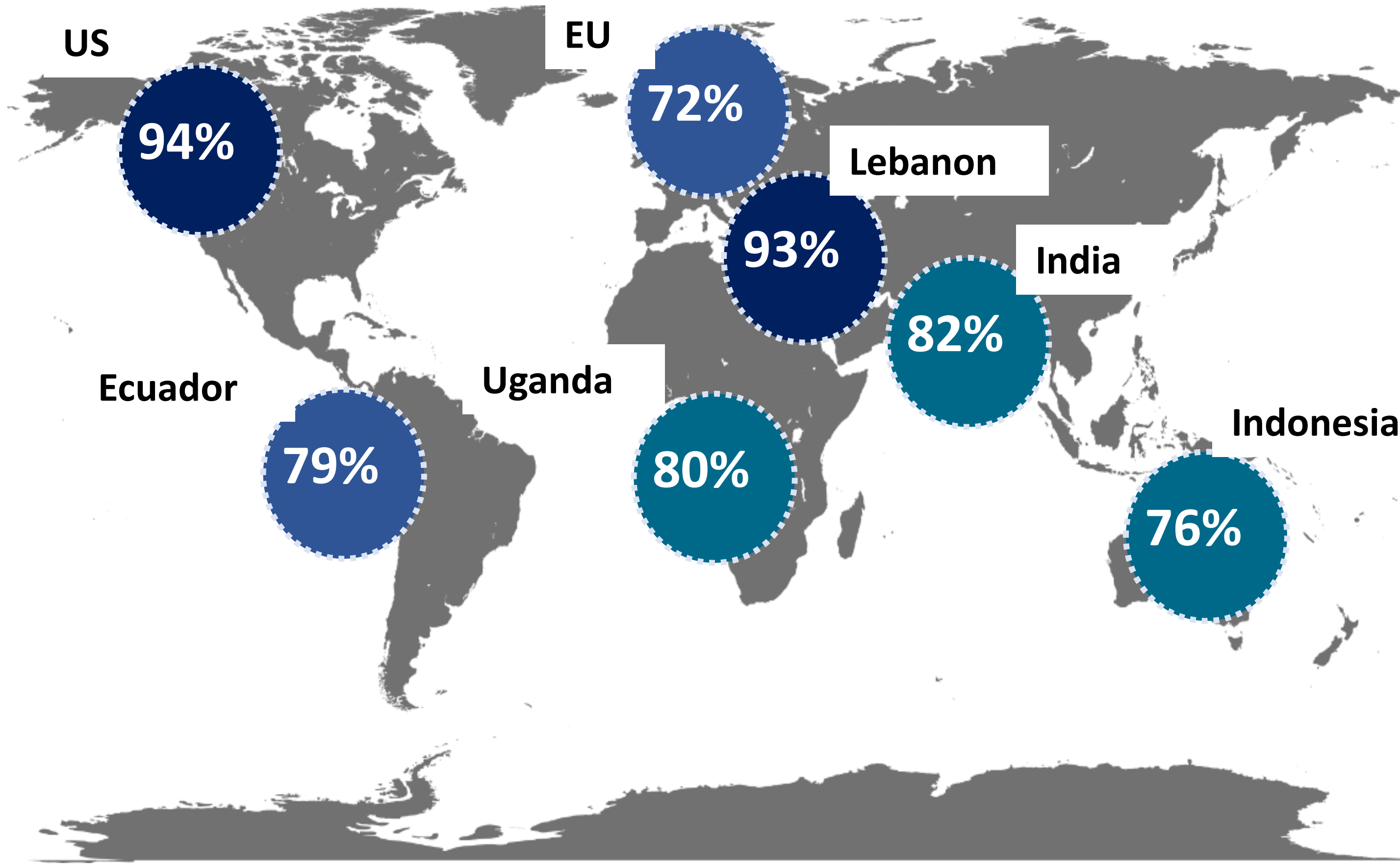


Figure 1. Percentage of tap water samples containing MPs according to the country(Picó and Barceló, 2019).

Picophytoplankton

General characteristics

- The size is generally defined as less than 2 μm(Vaulot *et al*. 2008).
- It is found in most freshwaters.
- *Synechococcus* sp. was dominant species in fresh water (Takasu *et al*. 2015;Callieri 2008).

Table 1 Abundance of picophytoplankton in freshwaters.

References	Picophytoplankton species	Season	Reservoirs
Wang *et al.*, (2004)	Picophytoplankton	Summer	Lake Donghu, China
Wang *et al.*, (2004)	Picophytoplankton	Summer	Lake Dongting, China
Carrick *et al.*,(2017)	*Synechococcus* sp.	Summer	Lake Superior, North America
Shi *et al.*,(2019)	*Synechococcus* sp.	Summer	Lake Fuxian, China

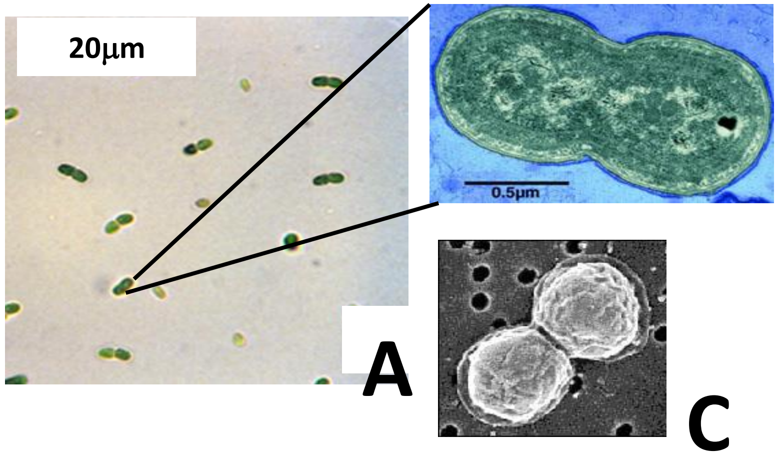


Figure 2. cell of *Synechococcus* sp
A was represented characteristic of cell exhibition in fresh water (University of Sevilla. B was represented cell structural(Waterbury et al. 1986)
And C was represented cell surface(The Institute for Research and Development).

Picophytoplankton removal

The coagulation method could remove picophytoplankton, but the removal efficiency was low (Aktas *et al.*, 2013).

Microplastics (MPs)

Size and shape

- Its are tiny plastic particles size is almost defined less than 5 mm(Rogers. 2022).
- Its are divided into two types.

Source

Primary → Industrial products material.

Secondary → The breakdown of larger plastics.

MPs removal efficiency via coagulation method

Reference	MPs size	Removal efficiency	Coagulant type, dose
Ma *et al.*, (2019)	<500 µm	20%	Alum, 0.74 mmol/L
Dorothy *et al.*, (2020)	1 µm-5 µm	93%	Alum, 20 mg /L
Wang *et al.*, (2020)	1 µm-5 µm	40%	ND

Figure 3 MPs contamination into freshwater (Badola *et al*. 2022).

The purpose of this research

In recent years, water purification problems due to fine particles such as picophytoplankton and microplastics have occurred.

In order to improve this problem, the relationship between aggregation and removal efficiency in the coagulation of fine particles, and the mechanism of coagulation inhibition were studied.

Then, based on these findings, an advanced coagulation method that improves the removal efficiency of fine particles was investigated.

Study framework

- Since the floc formation process in the coagulation of fine particles has not been elucidated, the coagulation process of fine particles was investigated from changes in the size distribution of flocs.

Chapter 3

Removal efficiency of picophytoplankton by using conventional coagulation method

Chapter 4

Comparative analysis of removal characteristics of fine particles in coagulation method.

- The formation of fine particles derived from coagulants that affect flocculation inhibition and the mechanism of inhibition by these particles were examined.

Chapter 5

Generation of aluminum particle in coagulation method.

- Based on above findings, an advanced coagulation method was investigated.

Chapter 6

Enhancement of coagulation method to remove fine particles.

Chapter 3

Removal efficiency of picophytoplankton by using conventional coagulation method

3.1 Background

- Previous studies have shown that there is a limit to the removal of picophytoplankton by conventional coagulation methods.

Research questions

- Why does the removal efficiency of picophytoplankton not increase even if the amount of coagulant dose is increased beyond the optimum amount of coagulant dose?

Research hypothesis

- When the coagulant is added in excess of the optimum dose, the coagulant does not react with the small size picophytoplankton, but the ratio of reaction with the large floc increases.

3.2 The purposes of this research

- The reason for the limit of removal of picophytoplankton by the coagulation method is analyzed based on changes in particle size before and after coagulation.

2. Material and methods

2.1 Artificial raw water

- **Picophytoplankton ; 1 NTU*, pH 7, Alkalinity 35 mg as $CaCo_3$.**

(*cell concentration approximately 20.1±0.5 × 10^5 cells/mL).

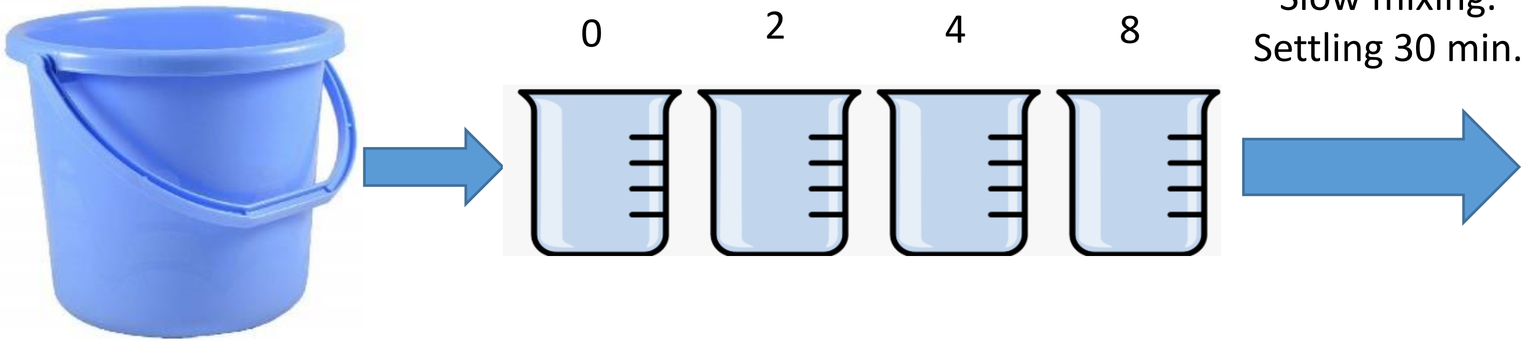
2.2 coagulation experiments

PAC was added at various doses (0, 1, 2, 4, and 8 mg/L) before rapid mixing.

Final pH was controlled 7 .
Initial alkalinity was adjusted 35 mg as $CaCo_3$.

PAC dose

Mixing ; rapid mixing
Slow mixing.
Settling 30 min.



Supernatants were taken to measure the **number of particles, size distribution, zeta-potential and turbidity.**

1 NTU of artificial raw water including PPP.

Figure 3.1 Diagram of coagulation experimental process. Jar-test were performed at room temperature (about 20 ±1°C) using a six-paddle stirrer.

2.3 Statistical analysis: Mean ± standard deviation (S.D.) and One Way ANOVA.

3.4.1 picophytoplankton removal efficiency by conventional coagulation method

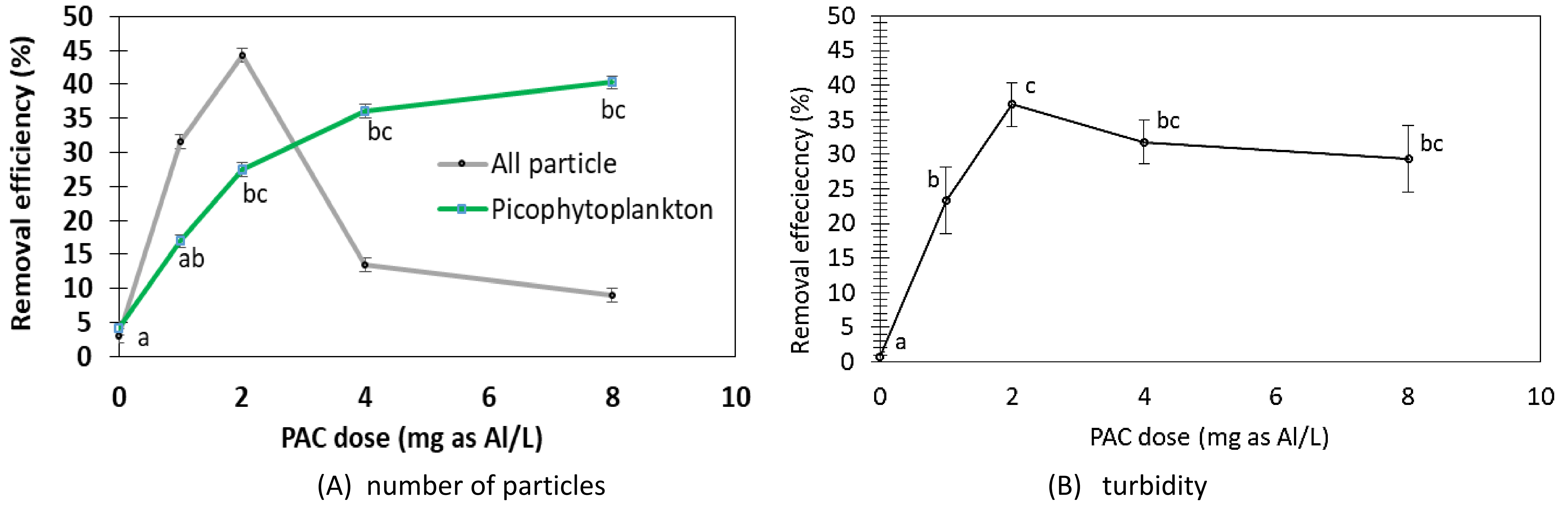


Figure 3.2. Removal efficiency by coagulation method evaluated by the number of particles(A) and turbidity (B)

- 2 mg as Al/L was the optimum dose for removing the number of picophytoplankton cells, which was similar to the conventional evaluation by turbidity(B).
- Increasing the PAC dose above the optimum dose decreased the removal efficiency of the number of all particles. Increase in the number of non living particles.

3.4.2 Removal efficiency for each particle size

- The more coagulants added (even beyond the optimum dose of 2 mg as AL/L), the lower the number of picophytoplankton in all sizes.
- Up to the optimum dose, the more coagulants added, the less the number of all particles in all sizes.
- Beyond the optimal dose, the more coagulant added, the greater the number of all particles of sizes 0.5-1 and 1-2 μm.
- It was found that when the coagulant was added in excess of the optimum dose, Non living particles with a size of 2 μm or less increased and did not act on the coagulation of picophytoplankton having the same size.

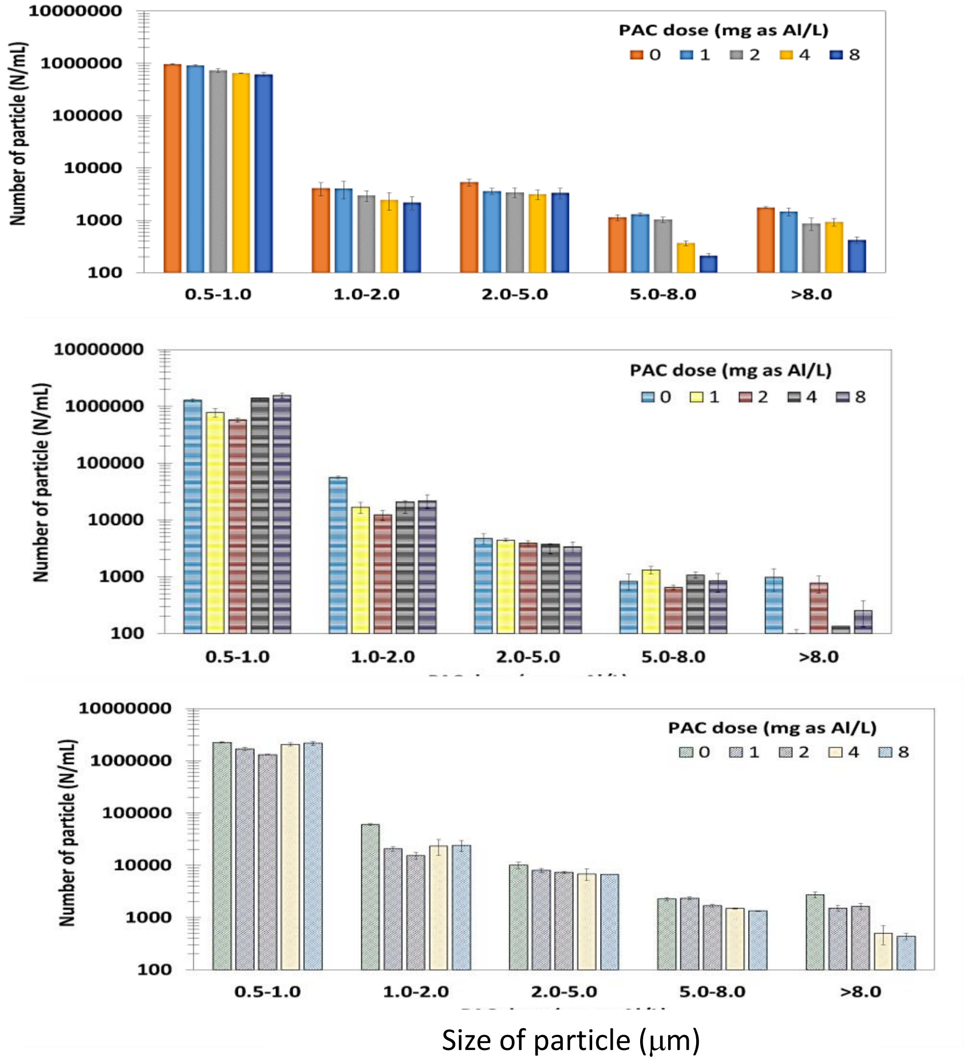
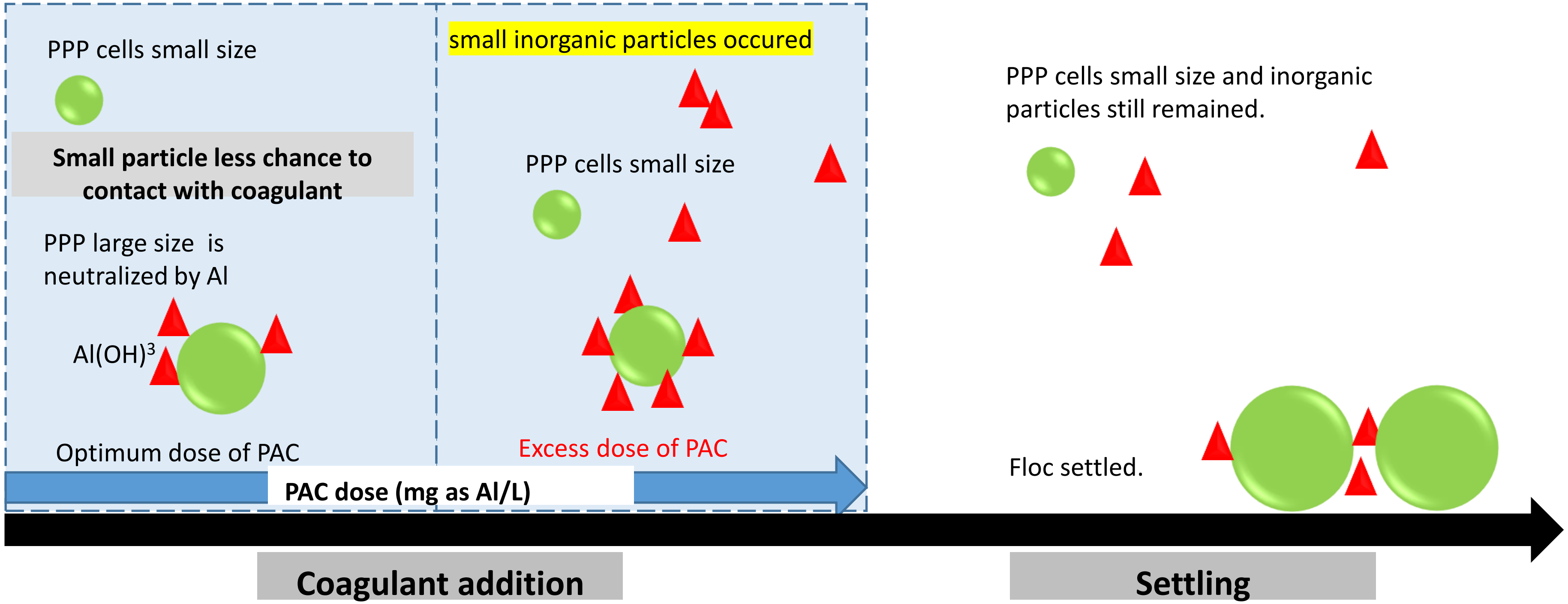


Figure 3.3. The number of picophytoplankton, **All particles, non living particle** per floc size remaining after coagulation and sedimentation.

- It is because the size of picophytoplankton was almost small size (0.5-1.0). Small particle less chance to contact with coagulant. (Lapointe et al., 2020; Zhou et al., 2021;Na et al., 2021).



3. 5 Conclusions

- The particle size 2 μm or less did not act on the coagulation.
- Moreover, increasing the PAC dose beyond the optimum dose increased the number of non living particles.

Chapter 4

Comparative analysis of removal characteristics of fine particles in coagulation method

4.1 Background

- Previous studies have shown that current water purification methods (coagulation, sedimentation, sand filtration) do not completely remove MPs and mix it into drinking water.

Research questions

- Why can't MPs be removed by conventional coagulation method?
- Is it because MP is as small as picophytoplankton and its density is also small?

Research hypothesis

- The reason why it is difficult to remove MPs by coagulation method is that they are small in size and low in density like picophytoplankton.

4.2 The purposes of this research

- The reason why MPs cannot be removed by the coagulation method is analyzed based on the change in particle size before and after coagulation and the comparison with kaolin particles with high particle density.

4.3 Material and methods

4.3.1 Particles

- Polystyrene (PS) particles were used as MPs. Turbidity standard solution II (Kanto Regents, for water quality test, 100 degrees) was purchased and diluted to a predetermined concentration before use.
- Kaolin (KL) particles were also used.

Figure 4-1. PS-containing solution

4.3.2 Artificial raw water

- MilliQ water ; number of particle was 20 N/mL, Turbidity was 0.0 NTU .
- PS or KL containing solution was added into MilliQ water.
- Final pH was adjusted to 7 by 0.01 M NaOH.
- Initial alkalinity was adjusted to 35 mg as $CaCO_3$.
- Initial turbidity ; 1 NTU.

4.3.3 Coagulation method

4.3.4 Evaluation of turbidity and particle size distribution

4.3.5 Statistical analysis

- Same as Chapter 3

4.4.2 Removal efficiency of KL and PS

- There was no significant difference between of turbidity removal efficiency and the number of particle **removal efficiency** at each coagulant dose (p-value> 0.05).
- Kaolin removal efficiency > PS removal efficiency. KL = 89% > PS = 30**%.**
- 2 mg as Al/L was the optimum PAC dose.

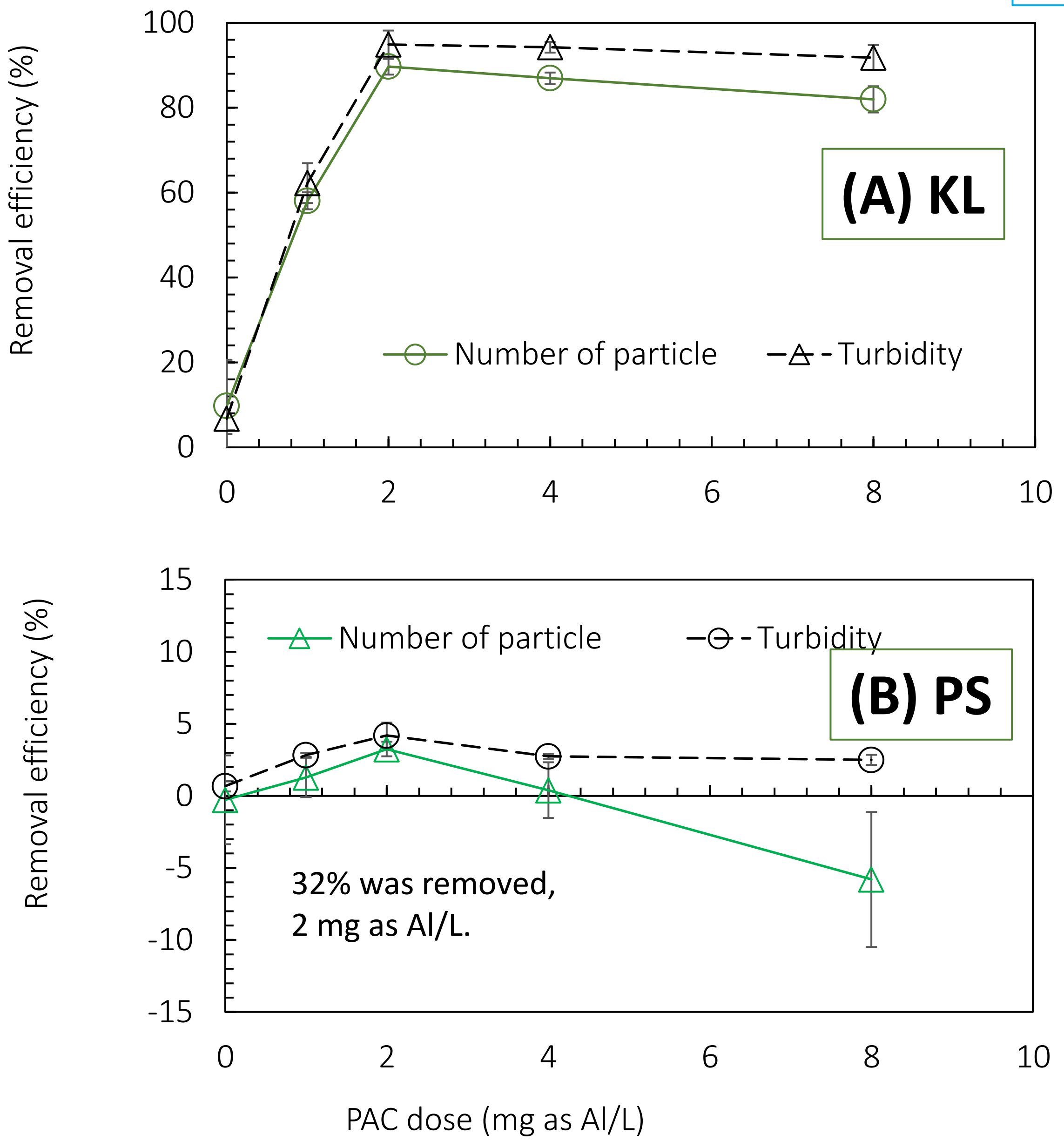


Figure 4-3. Effect of PAC dose on KL (A) and PS (B) removal efficiency

4.4.3 Residual number of particles for each particle size

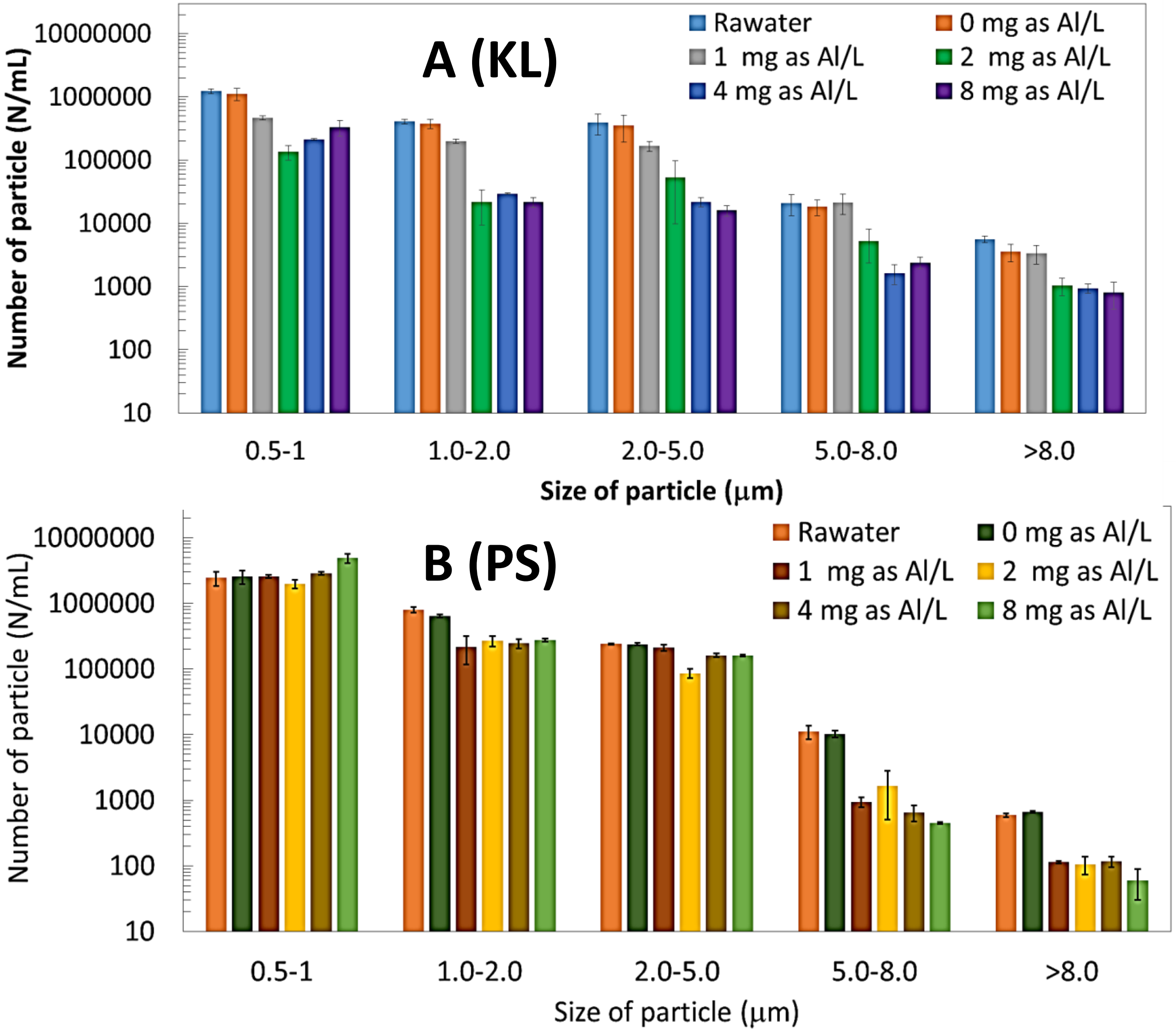


Figure 4-6. Number of KL (A) and PS (B) floc size remaining after coagulation and sedimentation

- Even in KL with a high removal efficiency, the number of KL particles with a size of 0.5-1.0 μm increased when the optimum dose of 2 mg/L was exceeded.
- In PS, the number of particles with a size of 0.5-1.0 μm increased when the optimum dose was exceeded. At the dose of 8 mg/L, the number of particles exceeded the initial number, which was due to the generation of particles derived from the coagulant.

The reason why the removal efficiency of MP is lower than that of KL in the coagulation method.

- Density PS = 1.05 g/cm^3 , KL= 2.65 g/cm^3
- Even with the same size, denser particles have more collisions than smaller particles(Jeffs *et al*., 1974; Kiorboe *et al,* 1990.)

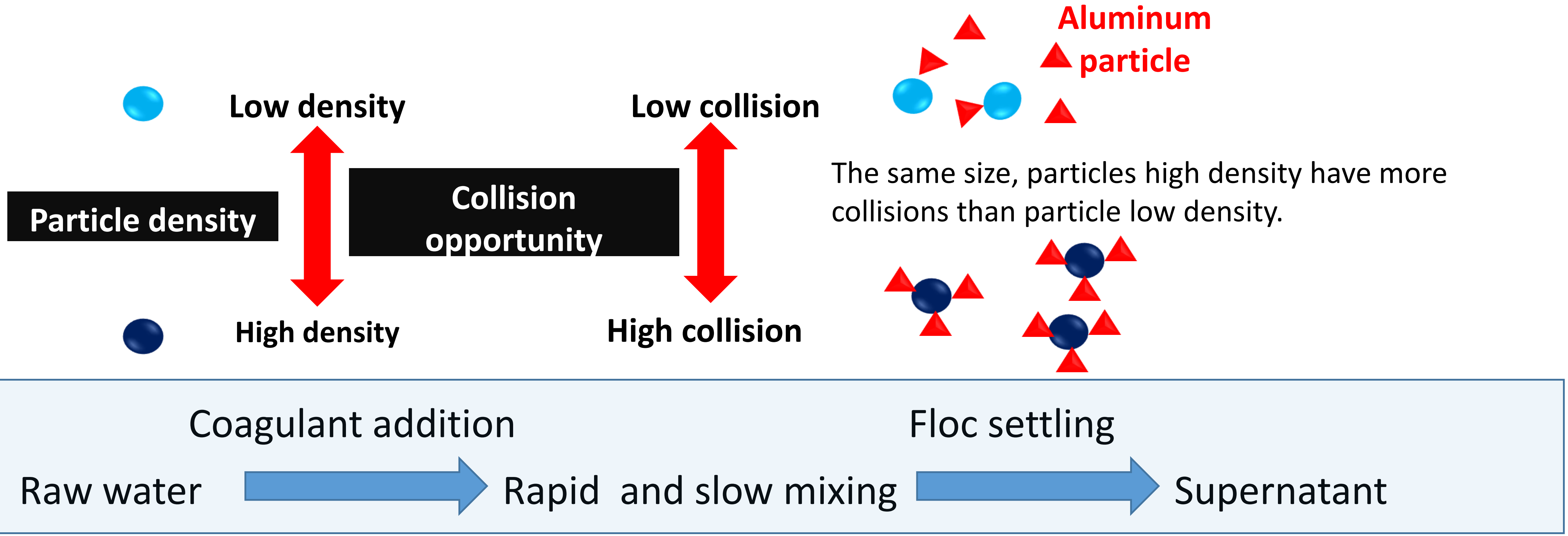


Figure 4-8. Diagram shown effect of particle density on collision opportunity in coagulation method.

Chapter 5

Generation of aluminum particle in coagulation method

5.1 Background

- Previous studies have shown that coagulant doses above the optimal dose cause an increase in turbidity. (Ogutu and Otieno, 2015; Takić et al. 2019)
- The reason is explained as redispersion, that is, the surface of the neutralized particles was positively charged and redispersed by the excessively added coagulant(Ramphal and Muzi Sibiya 2014).

Research questions

- Chapters 3 and 4 → In the region where the excess amount of flocculant was added, the decrease in the removal rate indicated by the number of particles was remarkable, and in some cases, it showed a negative value.
- Chapters 3 and 4 → It was thought to be due to the generation of aluminum particles, but until now no detailed investigation has been conducted.

5.2 The propose of this research

- Investigate the existence of coagulant-derived particles generated in the coagulation process and examine their role in coagulation.

5.3 Material and methods

5.3.1 Artificial raw water

- Milli Q water
- Dilute the PS solution to 1 NTU

5.3.2 Coagulation

- Jar-test (rapid mixing 100 rpm/5 min)

5.3.3 Acidification

- Water samples were taken after rapid mixing and adjusted pH below 3 by 0.1 N of HCl.

5.3.4 Indicators

- Turbidity
- Number of particles

5.4 Results and discussion

5.4.1 Effect of coagulant-derived particles on number of particles and turbidity

A coagulant was added to Milli Q water. Analyze the sample after rapid mixing.

- The number of particles tends to increase after the addition of coagulant. This is due to the particles derived from the coagulant.
- The addition of coagulant affects the increase in the number of particles, but there is no significant change in turbidity (p value> 0.05).

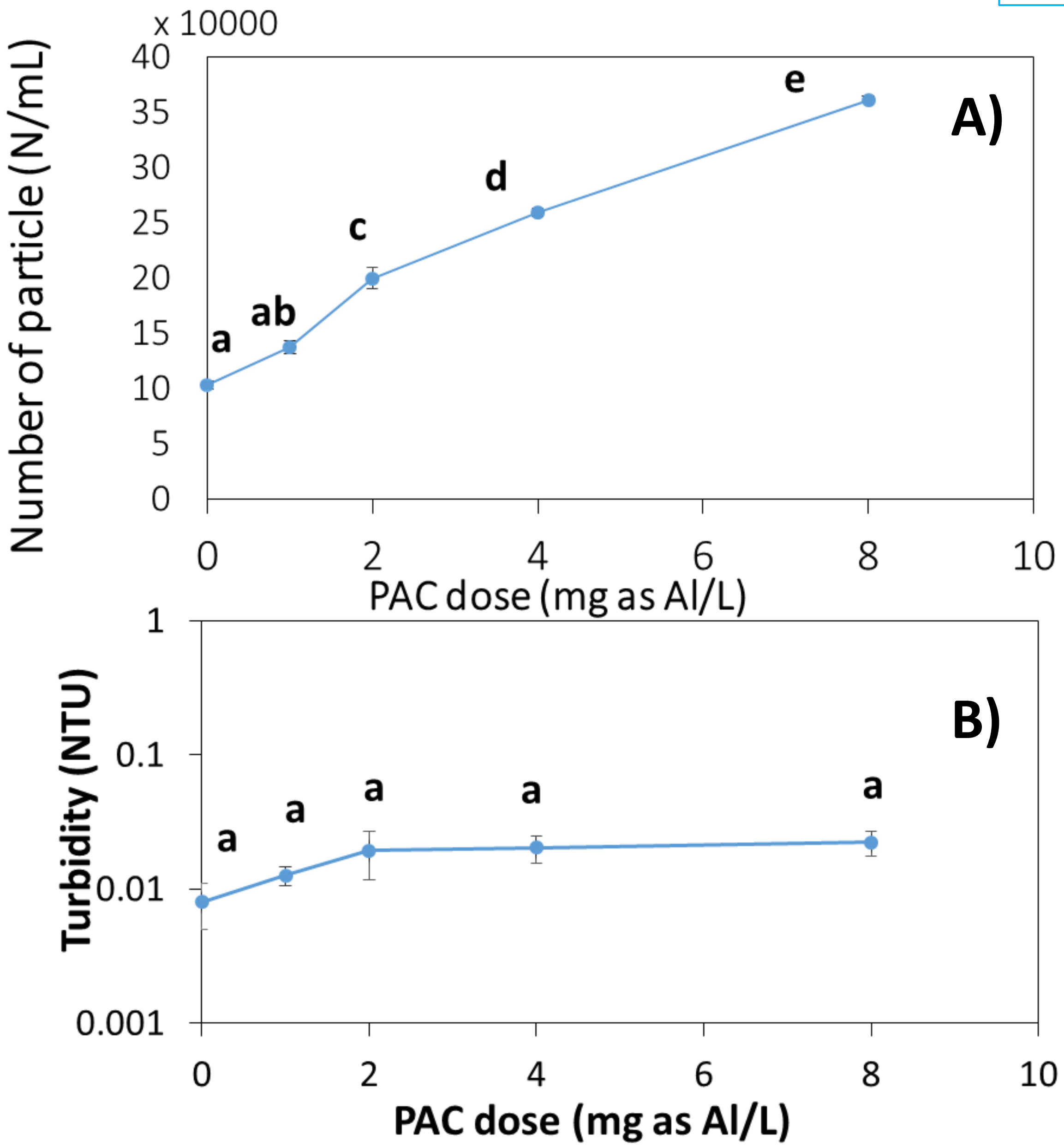


Figure 5-1. Changes in the number of particles (A) and turbidity (B) after the addition of coagulant

5.4.2 Effect of acidification treatment on the number of particles and turbidity.

Before and after acidification

- Upon acidification, the number of particles and turbidity were constant regardless of the amount of flocculant added.
- It was confirmed that the particles derived from coagulant could be eliminated by the acidification treatment.

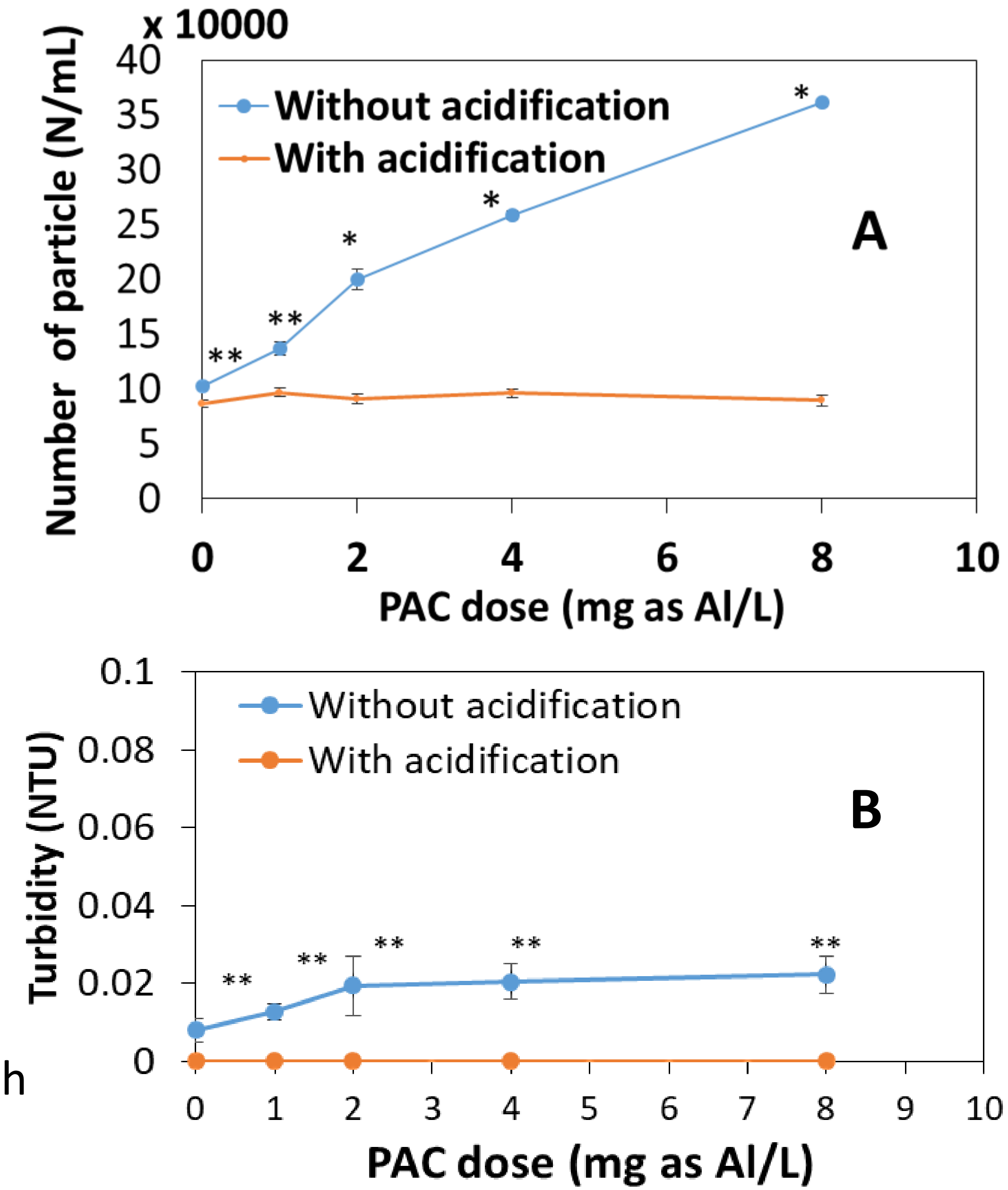


Figure 5-2. Effect of acidification treatment on number of particles (A) and turbidity (B) in coagulation.
*represent a significant difference in comparison between with acidification and without acidification (p-value <0.05).
** represent a non significant difference (p-value >0.05).

5.4.3 Effect of coagulant dose on the number of particles per particle size

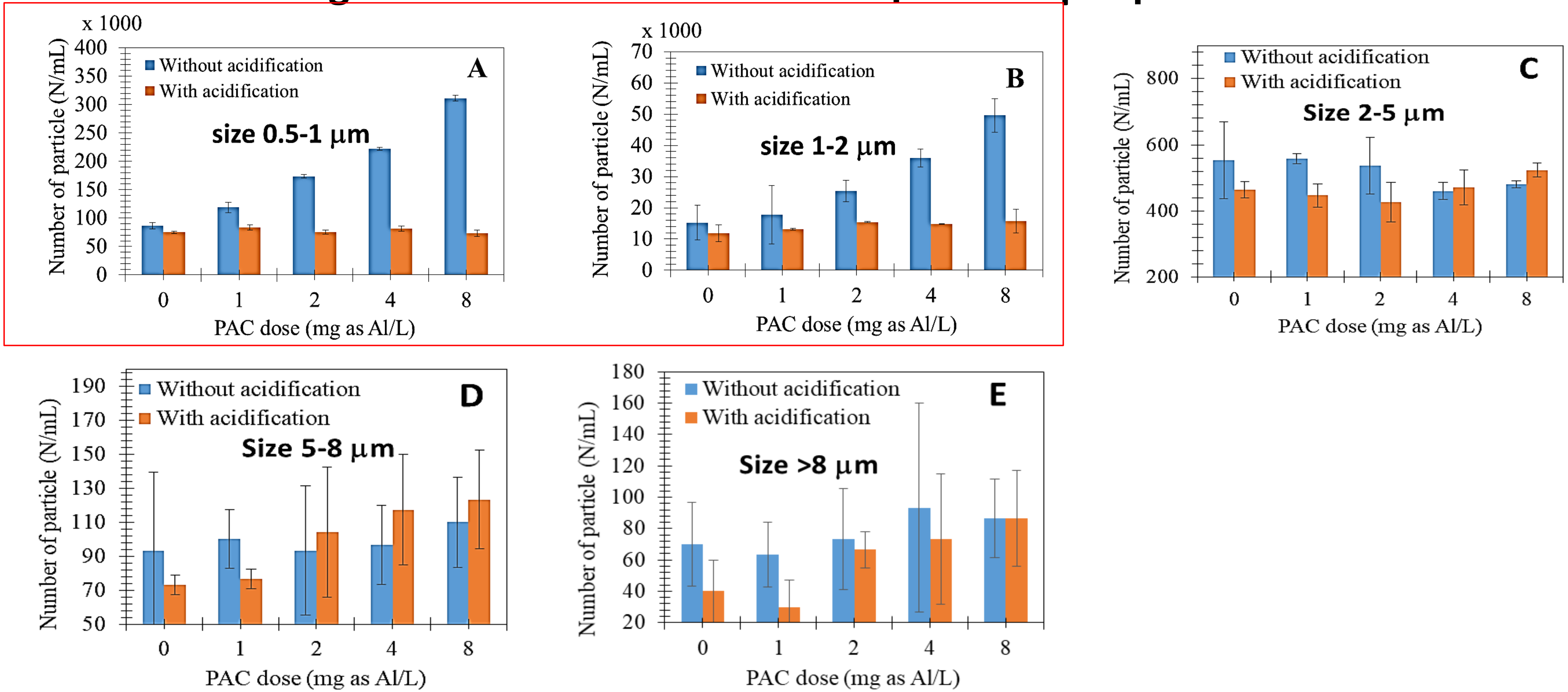


Figure 5-3. Changes in the number of particles for each particle size at each coagulant dose with or without acidification treatment

- The size of the coagulant-derived particles is 0.5-2μm.

Characteristics of coagulant derived particles

- As the results show, when PAC was added, aluminum particles were generated in milliQ water. The size of aluminum particles was 0.5 -2 μm.
- The results differed with previous research. Even though aluminum particle was not investigated directly but aluminum particle bond in coagulant is exceed (Duan and Gregory 2003) and size was 40 nm (Bradley,1993; Bottero 1987).
- In addition, turbidity measurements did not detect the generation of aluminum particles due to its small size (Ebie et al.(2006); Yao et al.(2014)).

Chapter 6

Enhancement of coagulation method to remove fine particles

6.1 Background

- **The results in Chapters 3 and 4 suggested that it is difficult to remove fine particles with conventional coagulation methods. In particular, the size was 0.5 – 1. 0 μm.**

- **The results also suggested that the overdosed coagulant did not react with particles of size 0.5 – 1.0 μm, but rather affected the increase in the number of particles.**

Research hypothesis

- The addition of kaolin improves the coagulation removal efficiency of fine particles (MPs and picophytoplankton).

6.2 The purposes of this research

- **Investigation of coagulation removal efficiency to remove fine particles by addition of kaolin. Insight into the mechanism of coagulation inhibition of fine particles.**

6.3.2 Kaolin addition experiments

KL solution(100 degree) were added at various doses (0, 2, 4, 5 and 10 mg/L) before rapid mixing.

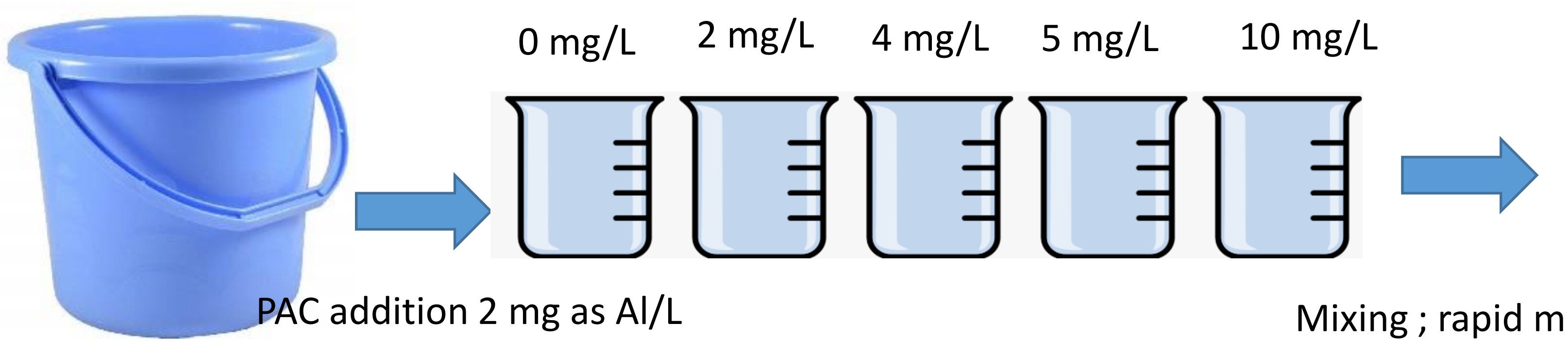


Figure 6-3. Diagram of kaolin addition experimental process.
Jar-test were performed at room temperature (about 20 ±1°C) using a six-paddle stirrer.

6.4 Results and discussion

6.4.1 Effect of kaolin addition on PS and picophytoplankton removal efficiency.

- The result showed that the addition of kaolin promoted PS and picophytoplankton removal. 4 mg/L of kaolin dose was the optimum.
- Since kaolin can be attributed to the high sedimentation performance due to increases floc size, which contributed to the number of particle and turbidity decreased(Aktas et al, 2012).
- In addition, the initial increase in turbidity and the high density of kaolin affect floc formation performance (Jeffs et al., 1974).
- However, with kaolin addition removal performance of PS was still higher than pico. Because density of picophytoplankton is lower than PS(Hu, 2014).

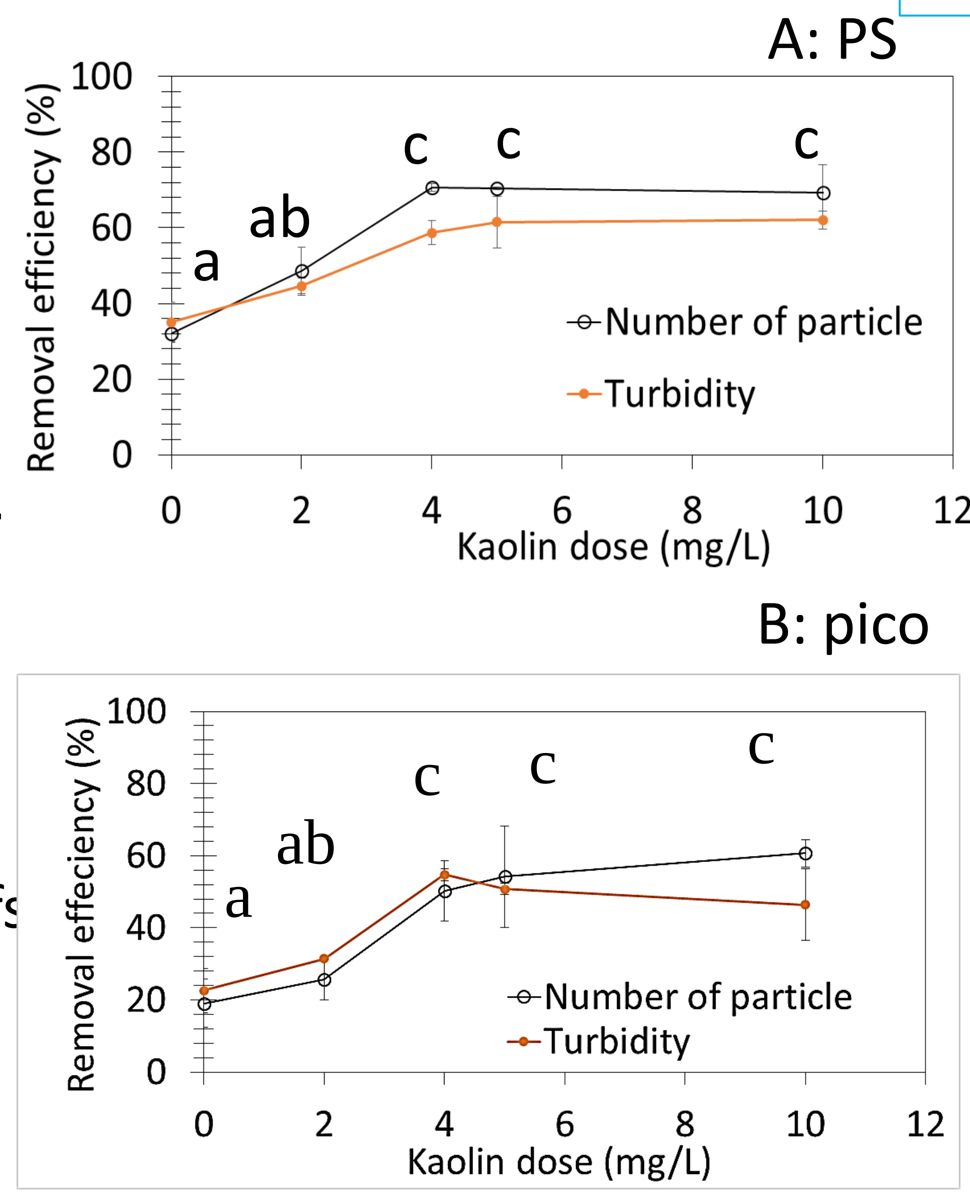


Figure 6-4. Removal efficiency of PS(A) and picophytoplankton(B) under various KL dose.

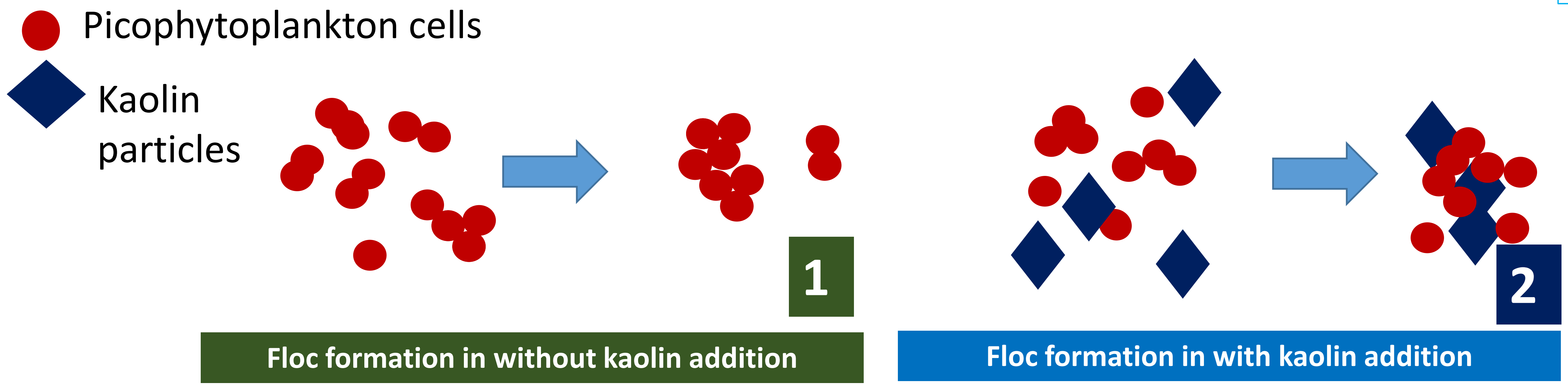


Figure 5 Diagram of floc formation, comparison between picophytoplankton cell (1)and additional kaolin(2).

- Since kaolin can be attributed to the high sedimentation performance due to increased floc size, which contributed to the number of particles and turbidity decreased(Aktas *et al*, 2012).
- In addition, the high density of kaolin affects floc formation performance by increasing <u>collision frequency</u> between particles with a coagulant(Jeffs *et al.*, 1974).

6.4.2 Effect of kaolin addition on changing of all particles and picophytoplankton particles.

- Adding kaolin 4 mg/L caused a significant decrease in picophytoplankton particles in the supernatant.
- However, increasing the KL dose effect on all particles increased, but the number of pico was not changed, pico couldn’t remove because PAC reacted with increased kaolin particles.

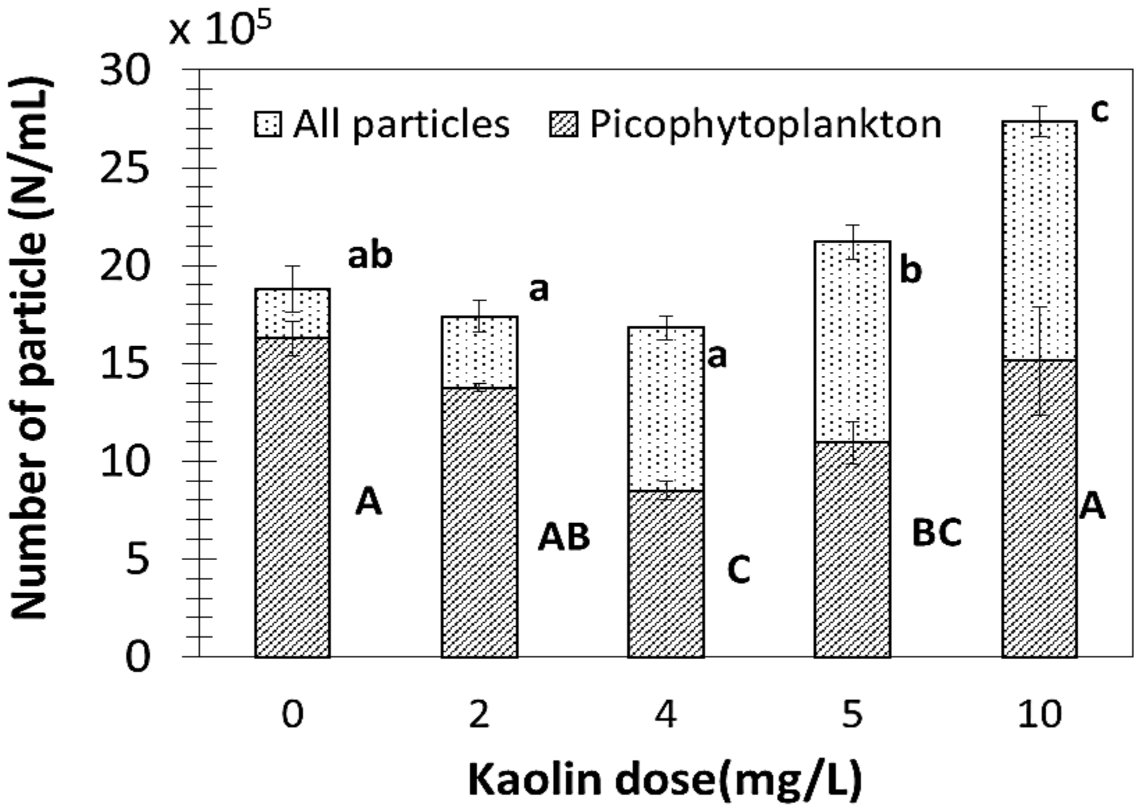


Figure 8 Effect of kaolin addition on changing of all particles and picophytoplankton particles. PAC dose is 2 mg Al/L. Same letter indicates no significant difference ($p<0.05$).

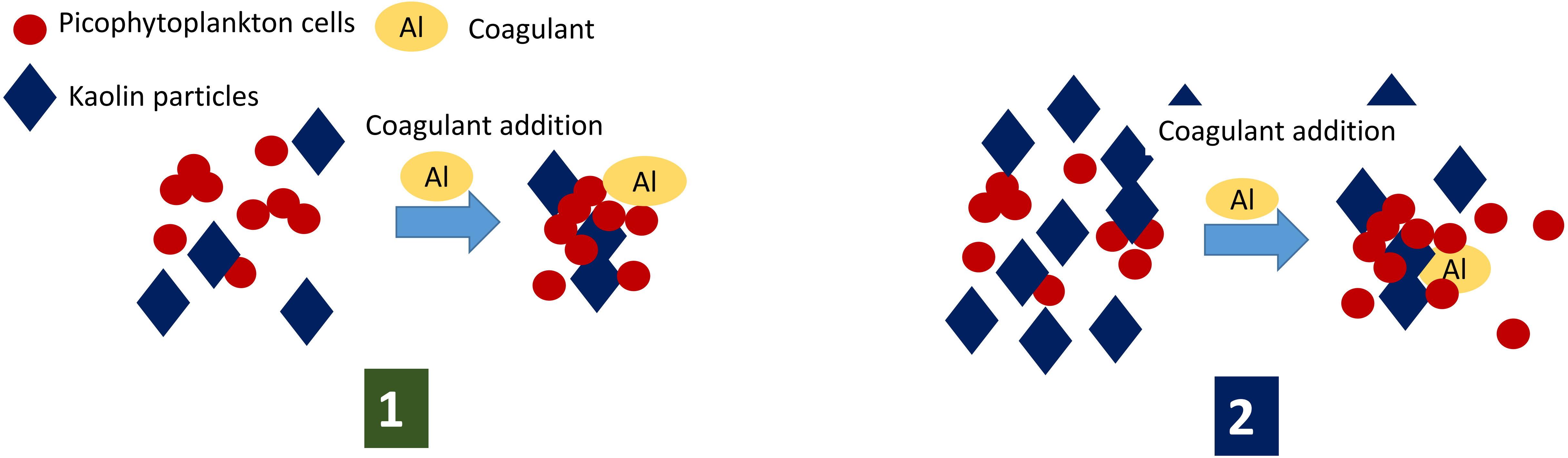


Figure 9 Diagram of floc formation, comparison between picophytoplankton cells (1)and additional kaolin (2).

- When the KL dose increased to 5 and 10 mg/L, picophytoplankton couldn’t remove because PAC reacted with increased kaolin particles.

4. Conclusions

Picophytoplankton cells were difficult to remove with the conventional coagulation method. This study used the kaolin addition method to enhance removal efficiency. As a result, it was found that the kaolin addition method was able to enhance picophytoplankton cell removal.

Chapter 7

Conclusions and Recommendations

7.1 General conclusions

1) Fine particles are difficult to remove with conventional coagulation method because they have little opportunity to come into contact with the coagulant and do not form flocs. In addition, the excessive addition of PAC produced aluminum particles with a size of 0.5 to 1.0 µm, which had the adverse effect of increasing the number of particles.

2) To enhance fine particles removal efficiency, kaolin addition method was used in this study. As a result, it was found that the efficiency of removing fine particles was improved.

7.2 Further research

1) **Development of a method for removing fine particles by an appropriate combination of a coagulant and an coagulant aid like kaolin.**

2) **Search for particles that aggregate better than kaolin to remove finer particles.**

3) **Picophytoplankton was still limited to be removed with the addition of kaolin and needs to be improved by other advanced methods.**


Thank you very much for your attention.
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