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Optimum Conditions for Enhancing Chitosan-Assisted Coagulation in Drinking Water Treatment

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Abstract: Coagulant aids are useful chemicals that enhance the efficiency of coagulation sedimentation treatment. For this purpose, it is necessary to choose safe chemicals to avoid various risks to the health of those who use the treated water. The use of chitosan, an abundant natural polysaccharide, as a coagulant aid is significant not only for safe water treatment but also for the effective utilization of unused natural water resources, which are mostly wasted. We experimentally determined the optimal treatment conditions for using chitosan as a coagulant aid in water treatment. The most efficient use was identified as adding chitosan at the stage of rapid stirring after the addition of coagulant accelerated initial dispersion. When used with the main coagulant polyaluminum chloride (PACl), the optimal concentration of chitosan was 0.8 mg L^{-1}, as estimated using the ζ potential showing isoelectricity at the optimal chitosan concentration. Determining the chitosan concentration using the minimum ζ potential was also valid for estimating the optimum concentration of chitosan, which is an extension of the method used at much higher turbidity, as seen in wastewater. Thus, the ζ potential-based prediction of the optimum chitosan concentration was effective even when the effect of sweep coagulation, which is normally induced at higher turbidity, was negligible. The superiority of using the coagulant PACl in combination with chitosan as the coagulant aid was demonstrated by comparing the in situ-observed coagulation process to cases with other coagulants and coagulant aids using direct time-series observation of the coagulation process. The use of chitosan with PACl was found to make the flocs easier to remove because it resulted in the largest mass fraction of the resultant floc sedimentation on the bottom of the vessel. In this study, using the PACl coagulant in combination with chitosan as the coagulant aid was found to be as viable as using the current popular combination of aluminum sulfate and polyacrylamide. Replacing polyacrylamide with chitosan contributed to reducing the potential risk to the health of those to use the treated water.

Keywords: coagulation; chitosan; coagulant aid; polyaluminum chloride; jar test

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1. Introduction

Coagulation sedimentation is widely used in water treatment because of its maintainability and low operation cost [1]. Processing drinking water largely depends on coagulation sedimentation, which accounts for approximately 5% of the total cost of running water treatment facilities [2]. The main part of the total cost includes various chemicals and processes such as coagulants, pH-adjusting agents, sludge treatment, and so on. In recent years, algal growth in water sources and contamination of raw water with natural organic matter (NOM) has increased the amount of coagulant use [3–5]. The increasing amount of coagulant use leads to water deterioration due to an increased concentration of residual aluminum. Therefore, the use of aluminum-containing coagulants should be minimized from an environmental viewpoint. The optimal use of coagulant not only reduces the total operational cost but also contributes to maintaining the quality of drinking water. Furthermore, reducing coagulant use can lead to a decrease in sludge generation.

Conventionally, iron and aluminum salts have been used for coagulation sedimentation, among which polyaluminum chloride (PACl) is most popular because of its superior performance under low-temperature conditions, minimal generation of residual aluminum moieties and sludge, and moderate impact on pH [6]. In Japan, PACl is predominantly used for water treatment. In recent years, high-basicity PACl has replaced the conventional basic PACl-based coagulants because it results in fewer residual aluminum moieties and has a higher removal efficiency of natural organic matter (NOM) [7].

Coagulant aids are effective chemicals that promote the growth of flocs and increase the efficiency of coagulation sedimentation. Sodium alginate (SA), activated silicic acid (ASA), and polyacrylamide (PAM) are typical examples that enhance sedimentation efficiency [8–10]. Coagulant aids help coagulants to effectively reduce turbidity and remove organic matter because an increased floc size results when these aids are used in combination with coagulants. In particular, PAM is widely used due to its high coagulation-assisting efficiency [11,12]. However, a disadvantage of PAM is that hydrolyzed monomers damage the human nervous system and are difficult to biodegrade [11,13]. Furthermore, a portion of PAM can facilitate the generation of disinfection byproducts (DBPs) when added to the disinfection process [14]. For this reason, non-toxic plant- or algae-based coagulants and coagulant aids have been investigated [13,15,16]. For example, Zhao et al. showed that the use of laminarin, a natural polysaccharide extracted from algae, effectively enhanced the cross-linking of microflocs and promoted floc growth, and laminarin was found to be as efficient as PAM [13]. Water treatment using natural chemicals contributes not only to a reduction in human health hazards but also helps to avoid environmental problems from the viewpoint of effective utilization of abundant natural resources. In the ongoing search for more environmentally friendly technologies, using chitosan as a coagulant aid is expected to play a significant role in water treatment. The abundance of polysaccharide chitosan that can be derived from deacetylated chitin in mushrooms and crab shells holds the greatest potential from a practical viewpoint [17]. Moreover, its environmental friendliness is also an advantage that should not be ignored in the present trend in technology. The abovementioned chemical substances are artificial commercial products, and thus there are often arguments on whether they should be used in the production of drinking water for the public. Chitosan has been shown to significantly contribute to coagulation, which suggests that it can be used in various industrial applications. Na et al. [18,19] successfully removed NOM and reduced trihalomethane formation potential (THMFP) by incorporating chitosan into PACl. The same mechanism is anticipated to remove natural inorganic matter since the physicochemical performance of chitosan in combination with PACl is not considered to be significantly different from those that facilitate the coagulation or aggregation of suspended tiny particulate matter composed of organic substances.

In general, coagulation sedimentation comprises dispersing coagulants in raw water followed by slow stirring to form flocs. Operational conditions significantly affect coagulation efficiency as well as various factors in raw water like pH, temperature, and NOM [20,21]. Particularly, the stirring condition influences both the reaction rate and resultant floc size [22–24]. The optimum coagulation condition when chitosan is used as the coagulation aid has not been established yet. The optimum working condition is not known because chitosan is not popularly used to treat relatively clean water in which much suspended solid matter is not present. Therefore, the potential usefulness of chitosan for water treatment is worth exploring to provide a technological basis for the upcoming generation. In order to verify the effectiveness of chitosan as a coagulant aid, the present study aimed to clarify its viable operational condition in combination with PACl. The objectives of the present study were (1) to determine the optimum stirring intensity [25], (2) to determine the optimum stage for adding chitosan, and (3) to determine the appropriate amount of chitosan to add to enhance coagulation efficiency.

2. Materials and Methods

2.1. Raw Water Sample

The raw water used in the experiments was sampled at Shitoki Dam in Iwaki, Fukushima Prefecture, Japan, on 12 November 2021. Table 1 lists the relevant parameters of the sampled water. The turbidity was relatively low (4.34 NTU) since the sampling date was in the middle of fall when algal growth was relatively dormant. The neutral state (pH 7.31) was consistent with algal dormancy. The turbidity of the sampled raw water was adjusted to 38 NTU $\pm$ 1 with kaolin. The baseline turbidity of the sampled water (4.34 NTU) was much lower than the set value (38 NTU). Thus, the overall turbidity after the adjustment was mostly dominated by the added kaolin, which is why the substances contained in the as-sampled water were intact, considering their effect could be ignored. Prior to the experiments, the pH value was adjusted to 7.5 $\pm$ 0.1. The temperature of the raw water was adjusted to (23 $\pm$ 1) °C before being used in the jar test experiments.

Table 1. Properties of the sampled water.

Condition	Value
Temperature (°C)	13.7
pH	7.31
Turbidity (NTU)	4.34
Alkalinity (mg L^{-1})	32.6

2.2. Chemicals

Polyaluminum chloride (PACl) (basicity 45–56%) and high-basicity PACl (basicity 67–75%) are commercially available coagulants and were provided by Taki Chemical Co., Ltd. (Hyogo, Japan). As a coagulant aid, chitosan was dissolved in 1 wt% hydrochloric acid to prepare a chitosan solution (1 mg L^{-1}). The commercially available polyacrylamide-based coagulant aid was provided by Mitsubishi Chemical Corporation (Tokyo, Japan). PACl (basicity 45–56%) was used as the standard coagulant with chitosan as the coagulant aid.

2.3. Jar Test Experiments

Jar test experiments were performed using beakers filled with 500 mL of raw water. A commercial jar tester (JMD-6E, Miyamoto Riken Co., Ltd., Osaka, Japan) equipped with 6 paddles was used for the direct observation of the floc formation process in all the experiments. In order to obtain a stably constant stirring rate, the same slot was used for all observational experiments with a precisely fixed position of the paddle. All jar test experiments were carried out on the same day in turn so that the ambient temperature could be kept constant throughout. PACl was added to each beaker by injection of its aqueous solution (20 mg L^{-1}). After injection, the water samples were stirred at the conditions listed in Table 2, followed by slow mixing at 45 rpm for 10 min. The supernatant water was removed after keeping the beaker still for 10 min until the completion of the overall sedimentation. The residual turbidity of the supernatant was measured for each sample (Turb430T, WTW, Germany). The ζ potential of the residual flocs suspended in the supernatant was measured (Model 502, Nihon Rufuto Co., Ltd., Japan).

2.3.1. Stirring Intensity

The GT value is generally used as a measure for stirring intensity, where G and T denote the velocity gradient and time, respectively [26]. The GT value is defined as below [27]

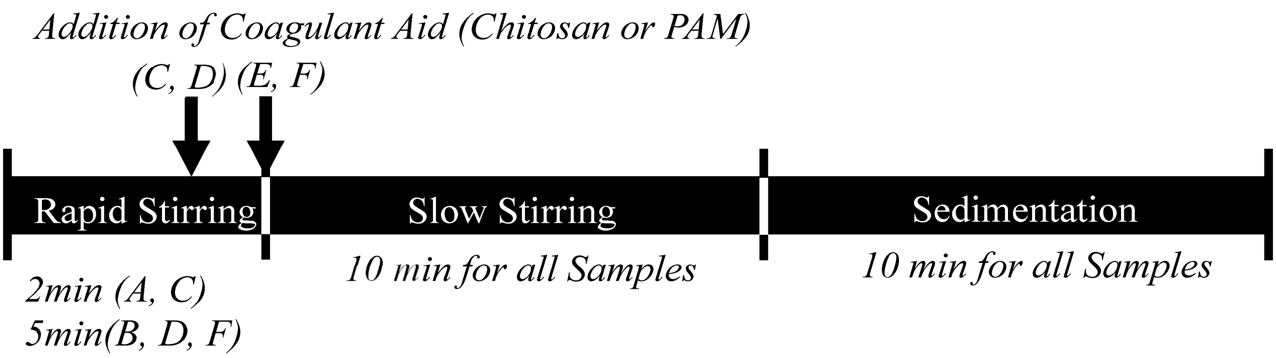
$$\text{GT value} \equiv \mathrm{T}\sqrt{\frac{CAv^3}{2\gamma V}}$$

where G: speed gradient (s^{-1}), C: stirring factor, A: area of the stirring blade (m^2), ν: peripheral speed of the impeller (m^2 s^{-1}), γ: kinematic viscosity (m^2 s^{-1}), V: stirring tank capacity (m^3), and T: stirring time (s).

T was set at 60 and 300 s, which correspond to GT30000 and GT135000, respectively. In the present study, the GT value was varied only with the duration of stirring T.

Table 2. Jar test conditions with temporal scheme (bottom).

		Rapid Stirring	**Chitosan**	
		GT Value $\times 10^3$	**Stage of Addition of Chitosan**	**Amount mg L^{-1}**
A	GT30	30	-	0
B	GT135	135	-	0
C	GT30-S0.5	30	Slow stirring as started	0.5
D	GT135-S0.5	135	Slow stirring as started	0.5
E	GT135-R0.5	135	Middle of rapid stirring	0.5
F	GT135-R0.8	135	Middle of rapid stirring	0.8



2.3.2. Optimum Stage for Adding Chitosane

To investigate the effect of the addition stage, chitosan was added before the rapid stirring stage or at the start of the slow stirring stage just after the rapid stirring stage, as described in Table 2. In the case that chitosan was added before the rapid stirring stage, the addition was carried out 4 min after starting the rapid stirring.

2.3.3. Effect of Chitosan Concentration

The effect of chitosan concentration on floc formation was investigated to elucidate the optimal concentration. In the jar test experiments, 0.5 mg L^{-1} and 0.8 mg L^{-1} were used as comparisons.

Furthermore, for obtaining auxiliary data to estimate the optimal chitosan concentration, the ζ potential of chitosan was measured at various concentrations. To carry out the measurements, 500 mL of raw water was stirred at 120 rpm for 5 minutes after adding 10 mg of standard PACl. Then, various amounts of chitosan from 0 to 0.75 mg were added, followed by 5 min of stirring. The ζ potential was measured for each sample.

2.4. Comparing the Performance of Various Coagulants

To demonstrate the high efficacy of standard PACl combined with chitosan as the coagulant aid, three other cases were tested using standard PACl alone, standard PACl plus the commercial acrylamide-based coagulant aid, and the high-basicity coagulant. For the comparative evaluation of the efficacy of the coagulants and coagulant aids, the scene of the whole coagulation process was recorded in 30 fps motion pictures until the 10 min-sedimentation was terminated. The resultant sedimented flocs were collected and completely dried at 50 °C for 15 min before observation using scanning electron microscopy (TM3030 Plus, Hitachi High-Tech Corporation, Tokyo, Japan).

3. Results

3.1. Effects of Stirring Intensity

Figure 1 shows the dependence of residual turbidity of the supernatant water after floc sedimentation on the stirring intensity (A vs. B) and the addition of chitosan (A vs.

C). The residual turbidity decreased from 2.8 NTU to 0.7 NTU by increasing the GT value from 30,000 to 135,000, which is more obvious than the effect of adding chitosan at the fixed GT value of 30000. Intensifying the stirring was shown to increase the coagulation efficiency (A vs. B), which was more obvious than the effect of adding chitosan during the slow stirring stage (B vs. C).

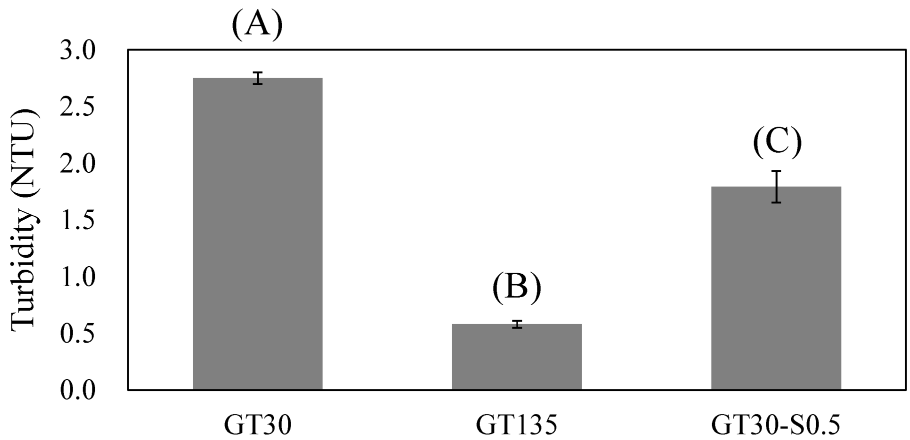


Figure 1. Effect of stirring intensity on residual turbidity. (A) GT30; (B) GT135; and (C) GT30-S0.5. Error bars indicate standard deviation ($n = 3$).

3.2. Effects of the Chitosan Addition Stage

Figure 2 shows the dependence of residual turbidity of the supernatant water after floc sedimentation on stirring intensity (C vs. D) and the stage at which chitosan was added (D vs. E). Intensifying the stirring positively contributed to enhancing the coagulation efficiency, as seen when chitosan was not used (Figure 1). Moreover, adding chitosan during the rapid stirring stage before the slow stirring stage resulted in greater sedimentation efficiency than when the addition was carried out during the slow stirring stage, which followed the rapid stirring stage.

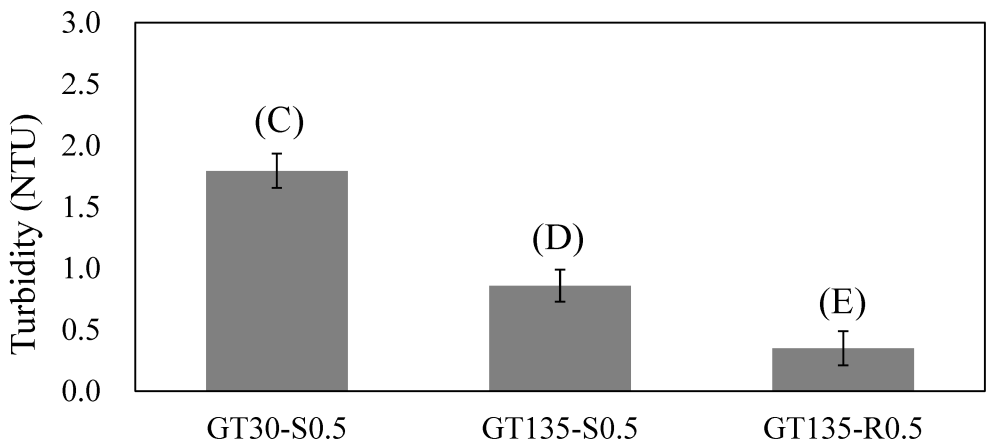


Figure 2. Effect of the stage at which chitosan was added on residual turbidity. (C) GT30-S0.5; (D) GT135-S0.5; and (E) GT135-R0.5. Error bars indicate standard deviation ($n = 3$).

3.3. Effects of the Amount of Chitosan Added

Figure 3 shows the dependence of residual turbidity of the supernatant water after floc sedimentation on the added amount of chitosan (E vs. F). In this comparison, chitosan was added during the rapid stirring stage in both cases, considering that the addition during the rapid stirring stage was already found to be more effective, as shown in Figure 2 (D vs. E). As more chitosan was added, the residual turbidity further decreased (E vs. F).

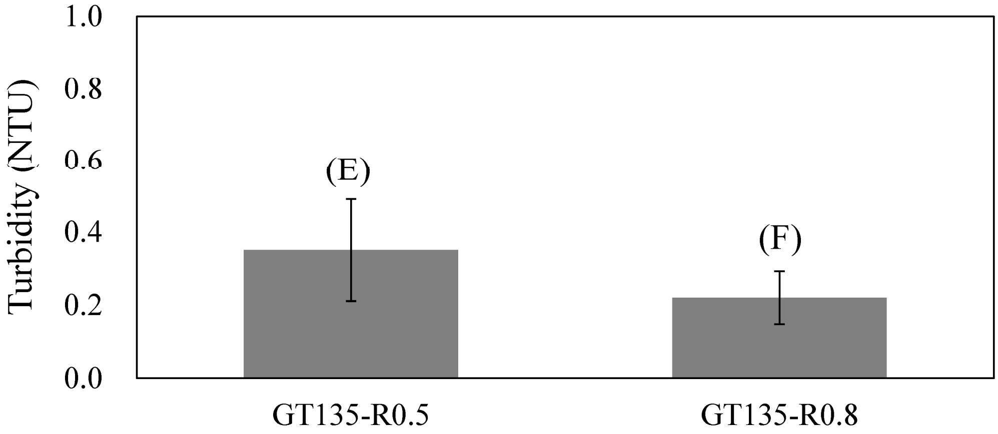


Figure 3. Effect of chitosan concentration on residual turbidity. (E) GT135-R0.5 and (F) GT135-R0.8. Error bars indicate standard deviation (*n* = 3).

Figure 4 shows a plot of the ζ potential of chitosan dissolved in water against its concentration, where the isoelectric condition was estimated to occur between 0.7 and 0.8 mg L^{-1}. The added amount of chitosan for sample F (0.8 mg L^{-1}) was determined based on this experimental result, which lead us to expect that floc coagulation would occur most easily at 0.8 mg L^{-1}.

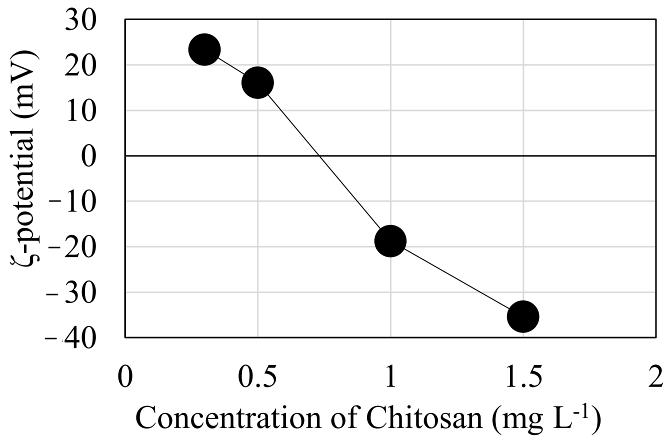


Figure 4. ζ potential of flocs against the concentration of chitosan.

As shown in Table 3, the ζ potential of sample F, which was the closest to zero, could be related to the lowest residual turbidity. On the other hand, the samples whose ζ potentials deviated relatively far from zero resulted in relatively higher residual turbidity.

Table 3. ζ potential of residual flocs suspended in respective supernatants.

Sample		ζ Potential (mV)
A	GT-30	−29.2
B	GT135	−29.6
C	GT30-S0.5	−29.7
D	GT135-S0.5	−13.5
E	GT135-R0.5	−9.5
F	GT135-R0.8	7.4

A comparison between samples C and D revealed that more vigorous stirring was more effective for bringing about the thorough dissolution of chitosan, which led to the ζ potential being closer to zero.

The experimental results stated above revealed that the GT value and the chitosan concentration of 135,000 and 0.8 mg L^{-1}, respectively, were optimum. In order to examine the viability of chitosan as the coagulant aid, the coagulation performance was comparatively evaluated between the present chitosan-incorporated condition and the cases where standard PACl, PAM-based commercial coagulant aid, and high-basicity PACl were used, respectively.

Figure 5 presents images of the floc formation obtained using the four kinds of coagulants at various durations after their addition (I: PACl, II: PACl+chitosan; III: PACl+commercial coagulant aid, IV: high-basicity PACl). Tiny flocs were observed to be formed in 4 min in all cases, after which the slow stirring stage was started. The most prominent difference was found when the commercial coagulant aid was used with standard PACl (III). The commercial coagulant aid worked best for forming the largest flocs in these four cases. For the other three, the overall appearance of the floc formation was similar (I, II, and IV), where the flocs were more uniformly formed than in (III). As seen in Figure 6, using chitosan as the coagulant aid resulted in earlier sedimentation (II) than in the cases where only PACl (I) and high-basicity PACl (IV) were used. This result was consistent with the promptest decrease in the residual turbidity (II), as shown in Figure 7, where it was approximately half compared with that in the absence of chitosan (I). The high-basicity PACl worked to an intermediate extent between the two cases with (II) and without (I) chitosan. The use of commercial coagulant aid, which led to the formation of the largest flocs, resulted in the highest residual turbidity. This seemingly irregular result could be ascribed to the generation of tiny flocs that are difficult to observe directly in the images in Figure 6III.

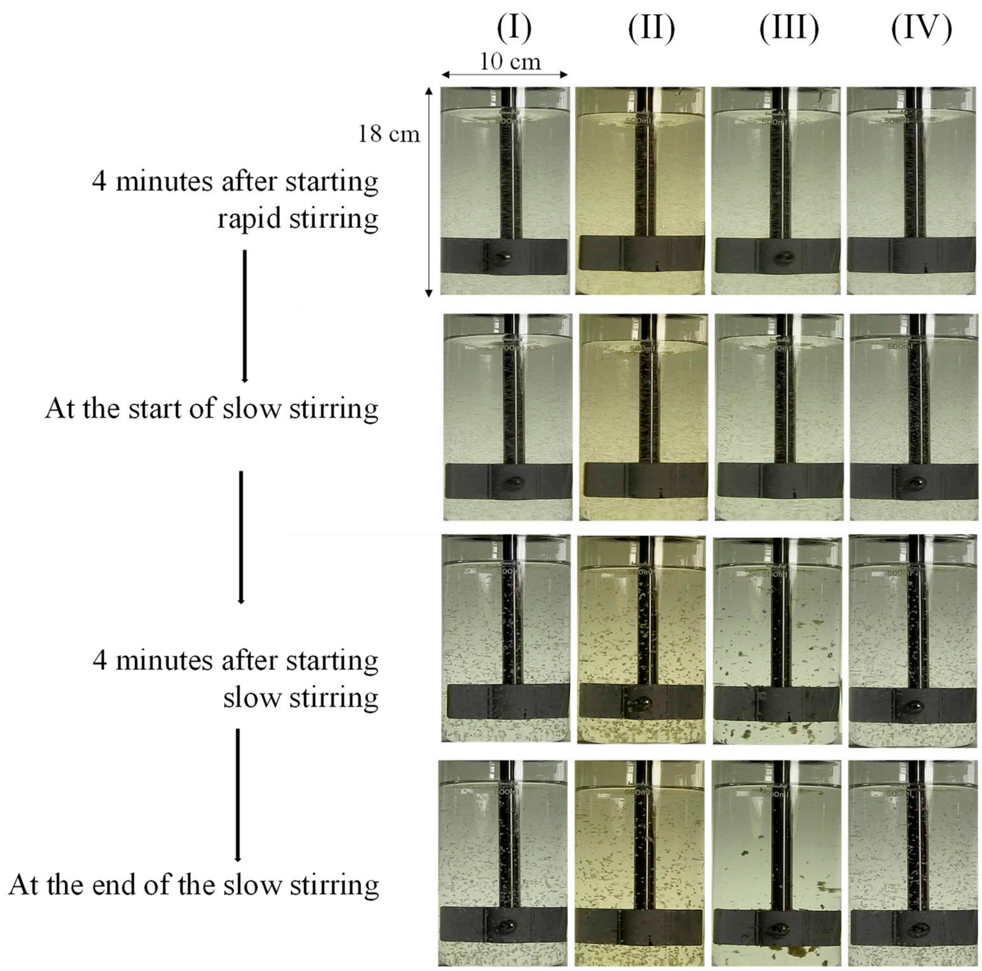


Figure 5. Images of beakers during the jar test experiment. (**I**) PACl; (**II**) PACl+chitosan; (**III**) PACl+commercial coagulant aid; and (**IV**) high-basicity PACl.

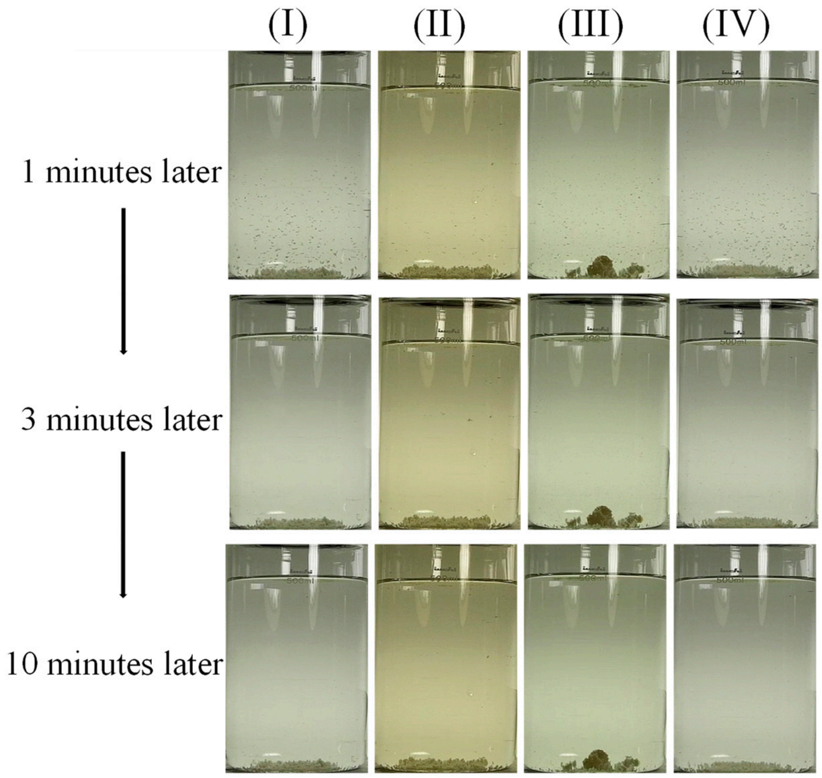


Figure 6. Images of beakers during sedimentation. (**I**) PACl; (**II**) PACl+chitosan; (**III**) PACl+commercial coagulant aid; and (**IV**) high-basicity PACl.

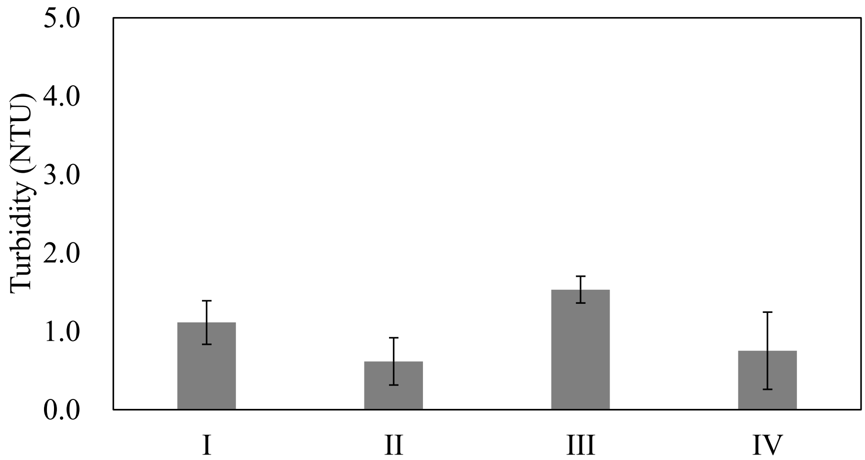


Figure 7. Residual turbidity after the jar test using various coagulants and coagulant aids. (**I**) PACl; (**II**) PACl+chitosan; (**III**) PACl+commercial coagulant aid; and (**IV**) high-basicity PACl. Error bars indicate standard deviation (n = 3).

Figure 8 shows a comparison of the magnified images of the sedimented flocs obtained using the above-mentioned four coagulants. The state of the coagulation of the constituent kaolin microparticles does not depend on the coagulant type that was used. The overall common texture of the flocs revealed that the coagulant type did not affect the coagulation process of the individual kaolin microparticles. The extent of the densification in the flocs was not particularly facilitated by the coagulant type or the presence of the coagulant aid used in the present study.

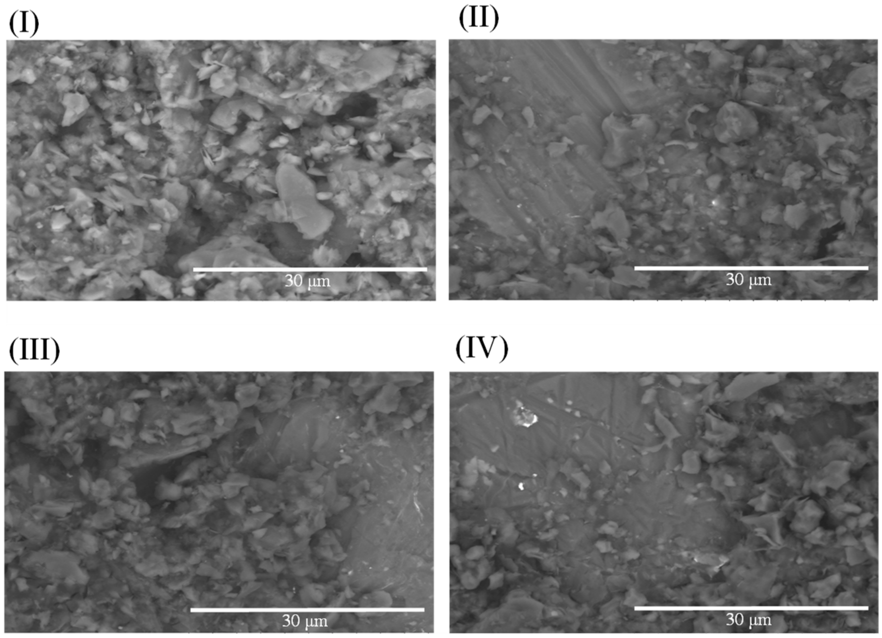


Figure 8. SEM images of flocs. (**I**) PACl; (**II**) PACl+chitosan; (**III**) PACl+commercial coagulant aid; and (**IV**) high-basicity PACl.

4. Discussion

4.1. Effects of Rapid Stirring for Prompt Dispersion of Chitosan as the Coagulant Aid

According to a study conducted by Lin et al., intensifying rapid stirring enhanced the inter-particle collision frequency, which facilitated the formation of larger microflocs [28]. Furthermore, microflocs formed during rapid stirring were less fragile as rapid stirring intensified [28–30]. These dual effects resulted in a continuous decrease in the residual turbidity with an increase in the intensity of rapid stirring. Considering the significantly positive influence of rapid stirring for quick dissolution of the coagulant, the same positive effect could be expected to contribute to enhancing the prompt and homogenous formation of the resultant flocs in the present study. Therefore, the effects of rapid stirring during which the coagulant aid was added were investigated from the viewpoint of efficiently decreasing the residual turbidity after the 10 min sedimentation.

According to Tambo, the collision frequency of dispersed microparticles increases with diameter and stirring intensity, which has been demonstrated in previous experimental studies [31]. Among various operational parameters, the GT value was found to be the most influential in minimizing the resultant residual turbidity [32]. In the present work, a larger GT value was found to be preferable for reducing the resultant residual turbidity, as seen in Figure 1. The positive effect of enhancing the GT value on reducing the resultant residual turbidity was irrespective of the presence or absence of chitosan as the coagulant aid. Thus, the GT value of 135,000 was regarded as superior to the GT value of 3000, and the former GT value was used thereafter in the present study.

Regarding the effect of the stage at which chitosan was added, addition before the rapid stirring stage was found to contribute more greatly to the reduction in the resultant residual turbidity than the case where chitosan was added before the slow stirring stage. This result indicates that the promptest dissolution of chitosan in the more incipient stage of sedimentation facilitated the intermolecular mutual contact or collision of the dissolved chitosan molecules. As a result, the decrease in residual turbidity was considered to have been induced more rapidly when chitosan was added before the rapid stirring stage than before the slow stirring stage (Figure 2).

4.2. Optimum Concentration of Chitosan as a Coagulant Aid

It was found that adding the chitosan aqueous solution at 0.8 mg L^{-1} led to a lower residual turbidity than at 0.5 mg L^{-1} (Figure 3). This result was consistent with the isoelectric condition seen in Figure 4. Thus, a chitosan concentration of 0.8 mg L^{-1} was considered to be the optimum concentration for coagulation sedimentation.

Furthermore, the measurement of ζ potential and the search for the isoelectric condition were found to be useful in determining the optimal concentration of the coagulant aid to be added to the sample water.

4.3. Effects of Chitosan as Coagulant Aid on the Removal of Kaolin Flocs

Generally, the formation of larger flocs is considered favorable for reducing the resultant residual turbidity [33]. However, minimum residual turbidity in the present study (Figure 7) was obtained not when the gigantic flocs were formed ((III) in Figures 5 and 6) but when chitosan was used as the coagulant aid in combination with PACl ((III) in Figures 5 and 6). Although the use of PAM as the coagulant aid obviously led to the formation of gigantic flocs, it did not result in minimum residual turbidity. This result showed that we could not predict the efficiency degree of the coagulant aid in removing the suspended flocs by sedimentation. Rossini et al. found that a rebound in the residual turbidity was possible due to the fragility of the gigantic flocs in shear flow [24], which could have been induced similarly in (III) in Figures 5 and 6.

Although the visible average size of the flocs depended on the species of the coagulants and coagulant aids, the SEM micrographs (Figure 8) showed that the overall microstructure of the flocs was similar irrespective of the species. Thus, predicting the degree to which the coagulant efficiency aids in coagulation sedimentation was impossible depending on the microstructure of the resultant flocs. It should be noted that enhancing the coagulation sedimentation based on the condition adjustment in terms of the ζ potential has been popularly implemented in wastewater with relatively high turbidity. Nevertheless, the result of the present study suggested that the ζ potential adjustment by adding chitosan at appropriate concentrations helped the formation of flocs and the reduction in the resultant residual turbidity.

In most cases, sweep coagulation is inefficient in drinking water treatment. However, it is possible to find the optimum operation condition for removing tiny, suspended solids from natural raw water by identifying the isoelectric condition for adding various contents of chitosan. In the present study, the most important finding was that the use of chitosan as a coagulant aid brought about the minimum resultant residual turbidity. This result implied that chitosan contributed to suppressing the formation of extremely tiny flocs, which could take an unacceptably long period during actual water treatment.

5. Conclusions

In order to demonstrate the practical viability of using chitosan as a coagulant aid for coagulation sedimentation-based water treatment, the effects of the addition of chitosan and its operational conditions for minimizing the residual turbidity were experimentally investigated. The conclusions of the present study are summarized in the following six points:

(1) Rapid stirring is preferable for increasing the rate of floc formation irrespective of the coagulant type and the presence/absence of a coagulant aid.
(2) Adding chitosan during earlier and more rapid stirring was favorable for facilitating floc formation, as indicated by the lower resultant residual turbidity.
(3) The optimum chitosan concentration for use as a coagulant aid was determined as 0.8 mg L^{-1}. This value could be justified in terms of the isoelectricity, where the electrostatic interfloc repulsive force was eliminated and further coagulation could be facilitated.
(4) The formation of gigantic flocs did not necessarily result in a minimized resultant residual turbidity. Although the use of chitosan as a coagulant aid did not lead to

the maximum floc size, the size uniformity caused by the presence of the dissolved chitosan seemed to have accelerated the decrease in residual turbidity.

(5) Searching for the isoelectric condition by varying the concentration of added chitosan was useful for finding the optimum chitosan concentration at which coagulation sedimentation occurs most efficiently to decrease residual turbidity. This method was shown to be effective even when the incipient turbidity was much lower than in wastewater, where the method of minimizing the ζ potential is commonly used.

(6) Using chitosan could mitigate the risk of polluting drinking water due to its harmlessness compared with using other artificial chemicals as the coagulant aid like poly-acrylamide. Considering the abundance and ubiquity of chitosan, it is a promising candidate natural resource that can replace artificial chemicals that have been used for treating drinking water.

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