Effects of addition sequence and rapid mixing conditions on use of dual coagulants

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S.H. Kim*, H.K. Kim, B.H. Moon**, G.T. Seo** and C.H. Yoon*****

*Civil Engineering Department, Kyungnam University, Korea (E-mail: *shkim@kyunganm.ac.kr*)

**Environmental Engineering Department, Changwon University, Korea

***Chemical Engineering Department, Kyungnam University, Korea

Abstract The performance of dual coagulants in clay suspension was investigated in this study using aluminium chloride and the cationic polymer as coagulants. According to the study results, the performance of dual coagulants was affected by dosage of aluminium chloride. Beneficial effect by use of dual coagulants were only noted when aluminium chloride was underdosed. The addition sequence of coagulants was important for the performance of dual coagulants. Simultaneous addition resulted in the best performance, while addition of the polymer first resulted in the worst performance. Addition of aluminium chloride first resulted in the similar performance as single use of aluminium chloride. Although sulphate ion improved the floc characteristics, similar results were obtained. The effectiveness of rapid mixing depended on dosage of aluminium chloride. Extending rapid mixing (6 min) was beneficial when aluminium chloride was underdosed so that coagulation occurred at the combination region. However, such benefit was not observed at the optimum condition, which belonged to the sweep coagulation region. Different floc formation caused the difference. Extended rapid mixing would be beneficial when collision between clay particles and Al(III) was necessary. However, such benefit would disappear at the optimum condition because rapid mixing could break up the floc already formed.

Keywords Addition sequence; Al (III); cationic polymer; dual coagulants; rapid mixing

Introduction

Inorganic coagulants of Al (III) and Fe (III) are the most popular coagulants at water treatment plant. Their effectiveness in removal of particles and organics are well established. Their problem lies in sludge production. Since a substantial amount of inorganic coagulants is usually required, a large amount of sludge is generated. Compared to such inorganic coagulants, a relatively small amount is required for cationic organic polymer. However, it usually performs well only in the narrow range of dosage.

Since inorganic coagulant and cationic organic polymer have their advantage and disadvantage, the combined use of them may result in the better performance than the single use of either one. Ammary and Cleasby (2004) investigated such possibility. They reported that dual coagulants outperformed the use of each coagulant alone at pH 7.8 or in the presence of 0.001 M sulphate at pH 6.0. Addition sequence was important in case of dual coagulants. They recommended adding the cationic polymer simultaneously with Fe (III). The simultaneous addition produced higher flocculation index values as well as higher resistance to shear.

Their study involved the use of Fe (III), which is not used in Korea. All water treatment plants in Korea rely upon Al (III), such as alum and polyaluminium chloride. This study, therefore, investigated the performance of dual coagulants in which Al (III) instead of Fe (III) was used as inorganic coagulant. This study focused effects of rapid mixing and addition sequence. Rapid mixing time was extended, and its effect on the performance of dual coagulants was investigated.

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Materials and methods

Clay suspension

Kaolin was used to prepare the clay suspension. After drying at 105 °C for more than 2 h, the predetermined amount of kaolin was dissolved in distilled water. The amount of kaolin was adjusted to make the turbidity of the suspension to become approximately 20NTU. Sodium bicarbonate was added to make the alkalinity of the suspension to be 1 meq/L (50 mg/L as $CaCO_3$). The pH of the suspension prepared in this method was approximately 7.8. The clay suspension was stored at the room temperature more than 5 h before use.

Coagulant

Aluminium chloride ($AlCl_3 \cdot 6H_2O$) was used as an inorganic coagulant in order to exclude any sulphate effect. Poly(diallyldimethyl-ammonium chloride) was used as the cationic organic polymer (Ciba Specialty Chemicals). Table 1 shows characteristics of the cationic organic polymer used in this study. The polymer was diluted at 0.2% before use.

Method

Rapid mixing was provided at 150 rpm for 2 min, and slow mixing was provided at 45 rpm for 15 min. Sedimentation of 30 min followed the slow mixing. When the addition sequence of coagulants was investigated, the first coagulant was added immediately after rapid mixing and the second coagulant was added 1 min after rapid mixing. Therefore, the first coagulant was given rapid mixing for 2 min, while the second was given for 1 min. When an effect of mixing time was investigated, rapid mixing time was extended up to 6 min.

A change in floc size after the coagulant addition was monitored using a photometric dispersion analyser (PDA). Floc size was monitored using the flocculation index (FI) value. Narrow light beam illuminates flowing suspension of particles in PDA. Then, random variation of number and size of particles in light beam causes the fluctuation in the transmitted light intensity. The transmitted light intensity consists of large component (DC) and small fluctuating component (AC). The root mean square value of AC divided by DC is termed as FI. The FI value increases greatly with aggregation. Detailed information about PDA and FI can be obtained elsewhere (Gregory and Nelson, 1984).

Floc (or aggregates) formed during coagulation and flocculation processes is recognised as fractal objects due to their fractal character. Fractal character implies that the mass of an aggregate (M) is related to the size (L) raised to a certain power (d_F), as shown in Eq. (1). Here, d_f is called "fractal dimension".

$$M \propto L_F^d \tag{1}$$

Floc shape of being regular or irregular was examined using fractal dimension. Fractal dimension was measured using PDA, as well as the small angle laser light scattering (SALLS) method in this study. According to this method, fractal dimension is closely related to the scattered light intensity, $I(Q)$, and light wave function, Q. Therefore, fractal dimension can be calculated using a log-log plot of $I(Q)$ and Q. Fractal dimension gives information about floc shape. A perfect sphere has a fractal dimension value of 3.

Table 1 Characteristics of the cationic organic polymer used in this study

Percentage of cation	Molecular mass	Diameter (nm)
100	$3–4 \times 10^4$	70*

*The diameter of the polymer in 0.5 M NaCl was quoted from Kim (2000)

An irregular-shaped floc has a less value, while a regular-shaped floc has a high value. Detailed information about SALLS and fractal dimension can be obtained elsewhere (Guan *et al.*, 1998).

$$I(Q) \propto Q_F^{-d} \quad (2)$$

Results and discussion

Coagulant saving by use of dual coagulants

Figure 1 shows the coagulation results of aluminium chloride: one at the optimum condition (A-15) and the other at the underdosed condition (A-7). The FI value increased rapidly at the optimum dosage, indicating the fast floc formation. The resulting floc was large, as reflected by the high value of the final FI (0.55). The large floc led to good settling and subsequently, the residual turbidity was low (1.80 NTU). On the other hand, the FI value slowly increased when aluminium chloride was underdosed. The resulting floc was small, as reflected by the low value of the final FI (0.35). The small floc led to poor settling, which was reflected by a relatively high value of residual turbidity (2.21 NTU).

Figure 1 also shows the performance of dual coagulants (S-7). The cationic polymer was added simultaneously together with 7 mg/L of aluminium chloride. A beneficial effect of dual coagulants was evident, as indicated by FI value. The use of dual coagulants produced a floc of which the final FI value was comparable to the value obtained by the single use of aluminium chloride at the optimum condition (15 mg/L). Similar residual turbidity value was also obtained (1.80 vs 1.83 NTU). These results indicate that the use of dual coagulants could reduce Al (III) consumption by more than half.

Although the floc size was large, the floc growth during the use of dual coagulants was not so fast. The floc growth was initially slow, similarly to the growth during the single use of aluminium chloride at the underdosed condition. However, the effect of dual coagulants was noted after about 10 min. A floc grew quickly so as for its final FI value to approach the value of 0.55.

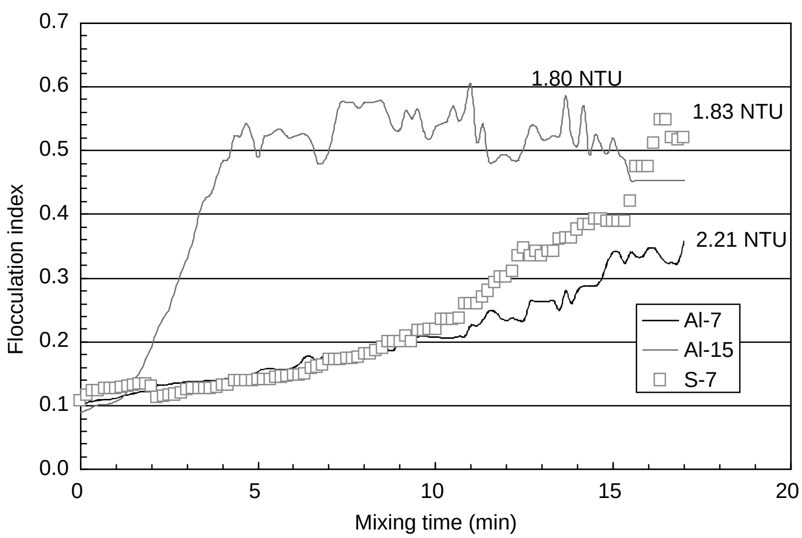

Figure 1 Comparison of single use of aluminium chloride with use of dual coagulants (aluminium chloride at 7, 15 mg/L and the cationic polymer at 0.07 mg/L)

According to the alum coagulation diagram (Amirtharajah and Mills, 1982), the optimum condition (aluminium chloride at 15 mg/L) corresponds to the sweep coagulation region. On the other hand, the underdosed condition (aluminium chloride at 7 mg/L) corresponds to the region at which combination of sweep floc and adsorption occurs. When aluminium chloride was dosed enough to reach the sweep coagulation region, the $Al(OH)_3$ precipitate formed instantaneously and quickly grew to a large floc. The situation was different when aluminium chloride was underdosed. Although the precipitate also formed at the combination region, the dosage was not sufficient to promote such quick formation of a large floc. The precipitates were subsequently small.

Rapid mixing effect

The above results suggest that rapid mixing effect would be different, depending upon the coagulation condition. When aluminium chloride was underdosed and coagulation occurred at the combination region, extended rapid mixing would be helpful because it could provide more opportunity for collision between small precipitates so that they could grow. On the other hand, when the dosage was sufficient and coagulation occurred at the sweep coagulation region, such beneficial effect would disappear.

In order to test the above hypothesis, rapid mixing was extended to 6 min. Its effect was examined at the combination region. Figure 2 compares the results at the extended rapid mixing of 6 min (RM6) as well as at the normal rapid mixing of 2 min (RM2). The suffix indicates coagulant used: Al indicates single use of aluminium chloride alone; S indicates use of dual coagulants. Effects of the extended mixing became conspicuous. First, the extended mixing expedited the floc formation. The floc growth was minimal even after 6 min with rapid mixing of 2 min. However, the floc growth was substantial after 6 min when rapid mixing was extended to 6 min. The FI value increased more than two-fold (0.16–0.39). Such benefit was also noted for the use of dual coagulants. The extended mixing increased the FI value even larger (0.45) at the use of dual coagulants. As mentioned earlier, the extended rapid mixing was beneficial because it could provide more opportunity for the particle collision.

Effect of chemical addition sequence

Chemical addition sequence was also important for the coagulant performance, as shown in Figure 3. Different sequences resulted in different floc formation. When two coagulants were added simultaneously (S), the floc grew faster. A large floc formed, as indicated by

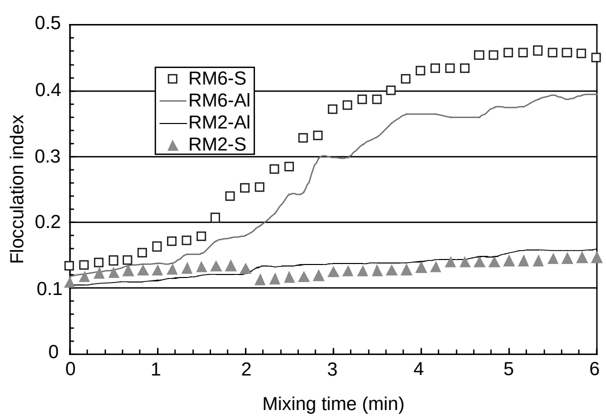

Figure 2 Rapid mixing effect (rapid mixing for 2 min and 6 min at aluminium chloride dosage at 7 mg/L and the cationic polymer at 0.07 mg/L)

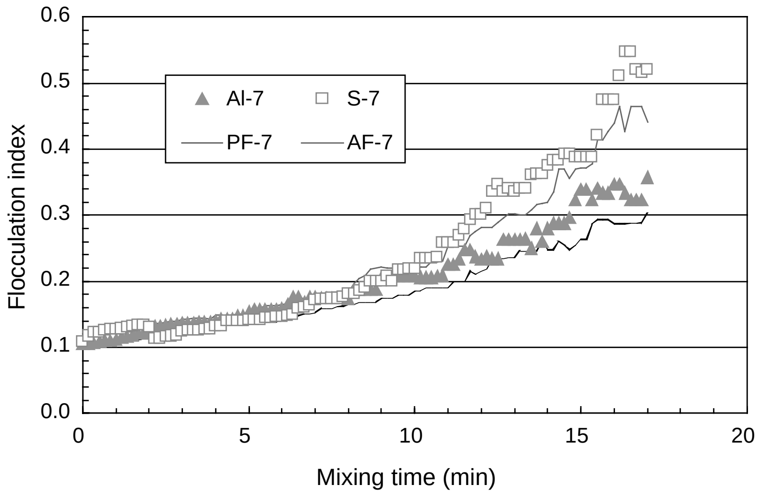

Figure 3 Effect of different chemical addition sequences (aluminium chloride dosage at 7 mg/L and the cationic polymer at 0.07 mg/L)

the high FI value. However, when the polymer was added first, and aluminium chloride was added later (PF), the floc formation was slow. The resulting floc was small, as indicated by the low FI value. When the addition sequences of the polymer and aluminium chloride were changed so that aluminium chloride was added first (AF), similar results as the addition of aluminium chloride alone (Al) were obtained.

The addition sequence also affected the floc shape. The floc formed at the simultaneous addition (S) was more regular-shaped than those formed at different addition sequences. According to Table 2, the floc formed at the simultaneous addition possessed the highest fractal dimension value (1.72) regardless of the coagulation condition. The simultaneous addition also produced the largest floc based on the FI value. These floc characteristics were reflected in residual turbidity. The lowest residual turbidity (1.83 NTU) was obtained at the simultaneous addition.

Figure 4 shows effect of the addition sequence at the optimum condition (15 mg/L). These results were different from those observed at the underdosed condition. The use of dual coagulants failed to outperform the use of aluminium chloride alone. The final floc sizes were all the same, regardless of the addition sequence. The kinetics of the floc formation was different depending on the addition sequence. The simultaneous addition (S)

Table 2 Residual turbidity and fractal dimension values under different coagulation conditions without sulphate (aluminium chloride at 7, 15 mg/L and the cationic polymer at 0.07 mg/L)

Aluminium chloride dosage	Addition sequence	Residual turbidity, NTU	Fractal dimension
7 mg/L	Al*	2.21	1.47
	AF**	2.08	1.50
	PF***	2.64	1.45
	S****	1.83	1.72
15 mg/L	Al	1.80	1.50
	AF	1.74	1.45
	PF	2.00	1.43
	S	1.67	1.80

*Al indicates addition of aluminium chloride alone
**AF indicates addition of aluminium chloride first and the polymer later
***PF indicates addition of the polymer first and aluminium chloride later
****S indicates simultaneous addition of aluminium chloride and the polymer

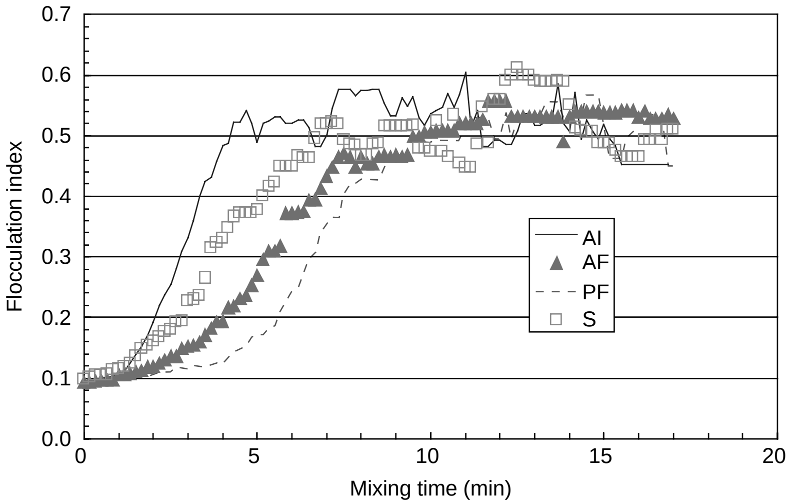

Figure 4 Effect of different chemical addition sequences (aluminium chloride dosage at 15 mg/L and the cationic polymer at 0.07 mg/L)

resulted in the fastest floc formation. Adding aluminium chloride first (AF) and the adding the polymer first (PF) followed. Nonetheless, the floc growth during use of dual coagulants was slower than that during single use of aluminium chloride (Al). It seemed that use of dual coagulants deterred the progress of the floc formation when aluminium chloride was added enough for the rapid formation of $Al(OH)_3$ precipitate.

Sulphate effect

Then, sulphate was added to the suspension in order to examine its effect. Preliminary experiments revealed (Kim *et al.*, 2004) that the best performance was obtained at a sulphate concentration of 15 mg/L (0.16 mM) for this raw water. Therefore, 0.16 mM of sulphate was added. Table 3 summarises the results. Sulphate improved the floc characteristics, which then led to the reduced coagulant consumption. The optimum dosage was 15 mg/L without sulphate, but it was 10 mg/L with sulphate. The lowest residual turbidity (1.02 NTU) was obtained at the dosage of 10 mg/L with the single use of aluminium chloride. However, similar results were obtained even with sulphate. The simultaneous addition (S) resulted in the best performance. It produced a big floc with regular shape despite aluminium chloride being underdosed. The final value of FI was approximately 0.7 and the fractal dimension was 2.18. The good floc characteristics led to the lowest residual turbidity (0.86 NTU).

The addition of aluminium chloride first (AF) produced comparable results to use of aluminium chloride alone at the optimum condition (10 mg/L). The final value of FI was

Table 3 Residual turbidity and fractal dimension under different coagulation conditions with sulphate of 15 mg/L (aluminium chloride at 5, 10 mg/L and the cationic polymer at 0.07 mg/L)

Aluminium chloride dosage	Addition sequence	Residual turbidity, NTU	Fractal dimension
10 mg/L	Al	1.02	2.03
5 mg/L	Al	2.22	1.60
	AF	1.00	1.94
	PF	1.54	1.58
	S	0.86	2.18

approximately 0.7 and the fractal dimension value was 1.94. The resulting residual turbidity was 1.00 NTU. The addition of the polymer first (PF) led to the production of the floc with poor settling characteristics. The floc was small with irregular shape. The final value of FI was 0.35 and the fractal dimension value was 1.58. Accordingly, the residual turbidity was relatively high (1.54 NTU).

Discussion

It seems that the mechanism of the floc formation would differ, depending on the addition sequence of coagulants. When aluminium chloride was added alone, coagulation would be governed by the $Al(OH)_3$ precipitate both at the sweep coagulation region and the combination region. However, the dosage was insufficient to promote the sweep floc formation at the combination region, and the floc growth was relatively slow.

When the polymer was added after aluminium chloride (AF), results were similar to the addition of aluminium chloride alone. In this case, the polymer would be added after the hydroxide precipitate had already formed. The polymer would then react with the precipitate rather than clay particles. If the polymer and the precipitate were charged oppositely, the polymer would be easily attracted to the precipitate. The floc formation would be expedited. Unfortunately, both the polymer and the precipitate were positively charged. The like-charge repulsion deterred their mutual contact. Any beneficial effect of dual coagulants became absent. That is the reason why AF yielded similar results as aluminium chloride alone. However, if there were clay particles remaining in the suspension, which were unaffected by the hydroxide precipitate, the polymer would be helpful.

The addition of polymer before aluminium chloride (PF) seemed to be the worst case because it deterred the formation of the hydroxide precipitate. The polymer first reacted with the negatively charged clay particles, which reduced the number of the nuclei available for Al (III) to precipitate. This deterred the formation of the hydroxide precipitate. The more nuclei there were, the faster the hydroxide precipitate formed. Since the polymer reduced the nuclei, precipitate formation was difficult. Simultaneous addition of aluminium chloride and the polymer (S) seemed to maximise the polymer effect. When they were added simultaneously, both reacted with clay particles. Addition of aluminium chloride would lead to the formation of the hydroxide precipitate, which would then enmesh some of the particles. The positively charged polymer would destabilise the negatively charged particles. The resulting product became non-ionic through charge neutralisation. The neutralised product could then be easily attracted to the hydroxide precipitate because the charge barrier was eliminated. Therefore, the floc formation was expedited and a large floc was produced.

The optimum dosage of aluminium chloride corresponded to the sweep floc region. The hydroxide precipitate formed instantaneously at this condition, and quickly grew to a large floc. Since the amount of the hydroxide precipitate was substantial, the polymer effect became negligible, regardless of the addition sequence.

Conclusion

The performance of dual coagulants in clay suspension was investigated in this study using aluminium chloride and the cationic polymer as coagulants. According to the study results, the performance of dual coagulants was affected by dosage of aluminium chloride. The use of dual coagulants effectively reduced Al (III) consumption by more than half when aluminium chloride was underdosed. However, such beneficial effect was absent at the optimum conditions. The addition sequence of the coagulants was important for the performance of dual coagulants. Simultaneous addition resulted in the best performance, while addition of the polymer first resulted in the worst performance. Addition of aluminium chloride first resulted in the similar performance as single use of aluminium chloride. Different coagulation mechanisms caused the difference. The polymer helped the Al (III) coagulation in case of the simultaneous addition, because both could react with clay particles. However, the polymer hindered the Al (III) coagulation by reducing nuclei for the hydroxide precipitate in case of the addition of the polymer first. Although sulphate improved the floc characteristics, similar results were obtained.

The effectiveness of rapid mixing depended on dosage of aluminium chloride. Extending rapid mixing to 6 min was beneficial when aluminium chloride was underdosed so that coagulation occurred at the combination region. However, such benefit was not observed at the optimum condition, which belonged to the sweep coagulation region. Different floc formation caused the difference. Extended rapid mixing would be beneficial when collision between clay particles and Al (III) was necessary, as when aluminium chloride was underdosed. However, such benefit would disappear at the optimum condition because rapid mixing could break up the floc already formed.

Acknowledgements

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