Environ. Eng. Res. Vol. 10, No. 3, pp. 105~111, 2005
Korean Society of Environmental Engineers

ENHANCED COAGULATION: DETERMINATION OF CONTROLLING CRITERIA AND AN EFFECT ON TURBIDITY REMOVAL

Seung-Hyun Kim†
Department of Civil Engineering, Kyungnam University, Masan, Korea
(received November 2004, accepted April 2005)

Abstract : The applicability of the USEPA's (United States Environmental Protection Agency) three criteria of enhanced coagulation (criterion I-TOC level less than 2 mg/L before chlorination; criterion II-% requirement of TOC removal; criterion III-point of diminishing return) for Korean waters was evaluated in this study. This study also investigated an effect of enhanced coagulation on turbidity removal, and attempted to identify the best coagulant for enhanced coagulation. Three different waters were used in this study: one river water and two lake waters. Five different coagulants were used: alum, liquid alum, PACl, ferric chloride with and without water. Results of this study showed that all three criteria were achievable for the tested waters. For these waters, controlling criterion was found to be different depending upon raw water characteristics. When initial TOC level was low (< 4 mg/L), criterion I (< 2 mg/L) could be the controlling criterion. As TOC level increased, criterion II (% TOC removal) became the controlling criteria. It was possible to achieve different goals of turbidity and TOC removals. Although the optimum region of TOC removal was more acidic than that of turbidity removal, there was no conflict between these two removals. The best coagulant was found to be different depending upon the evaluation tool: maximum and optimum removal. Ferric chloride was more effective than alum in terms of the maximum TOC removal, while Al-based coagulant such as alum or PACl was the best coagulant in terms of the optimum TOC removal.

Key Words : enhanced coagulation, controlling criteria, turbidity removal, best coagulant, optimum TOC removal

INTRODUCTION

Coagulation has traditionally targeted to remove particles in water. The situation has changed with time, and more than particle removal is now required for coagulation. Coagulation often acts as a barrier against natural organic matter (NOM). NOM causes color, increases coagulant and oxidant demands, serves as a substrate for biological growth in distribution system, and more importantly serves as a precursor to potentially harmful disinfection by-products (DBP).[1,2] The main purpose of NOM removal used to be color,[3] but the focus has been recently shifted to DBP since the discovery of THM (trihalomethane). There is also a considerable interest in DBP in Korea. Korean drinking water standard currently regulates eight species of DBP: TTHM (total trihalomethane), chloroform, chloral, dibromoacetonitril, dichloroacetonitril, trichloroacetonitril, and haloacetic acid (HAA) in treated water.[4] Of these, TTHM and chloroform should be less than 0.1 mg/L and 0.08 mg/L, while HAA in the sum of dichloroacetic acid and trichloroacetic acid should be less than 0.1 mg/L.

† Corresponding author
E-mail: shkim@kyungnam.ac.kr
Tel: 055-249-2671, Fax: 055-249-2664

When a role of coagulation is expanded to include NOM removal as well as particle removal, it is called as "enhanced coagulation".[2] Since enhanced coagulation is now listed as the best available technique to reduce NOM, USEPA requires water treatment plants to practice enhanced coagulation through the Disinfectant & DBP rule. They provided three criteria for enhanced coagulation: 1) criterion I-TOC level less than 2 mg/L before chlorination; 2) criterion II-% requirement of TOC removal determined by TOC-alkalinity matrix; 3) criterion III-point of diminishing return (PODR). Water treatment plants must satisfy one of these criteria. Table 1 shows the TOC-alkalinity matrix. Detailed information about these criteria can be found elsewhere.[2]

Table 1. Characterization of raw water and % requirement of TOC removal by TOC-alkalinity matrix

TOC concentration, mg/L	Alkalinity concentration, mg/L as $CaCO_3$		
	0~60	60~120	>120
2~4	LL[1] (40)[2]	LM (30)	LH (20)
4~8	ML (45)	MM (35)	MH (25)
>8	HL (50)	HM (40)	HH (30)

[1]the front letter indicates TOC level, and the second letter indicates alkalinity level; L stands for low level, M stands for medium level, and H stands for high level

[2]Values in parentheses indicate the minimum % TOC removal required by TOC-alkalinity matrix.

Enhanced coagulation is not a requirement in Korea, and no criterion is yet available. However, it is quite possible that enhanced coagulation is included in the future regulation due to a considerable interest in DBP. This study is therefore planned to provide information for the future regulation. More specifically, this study attempted to examine the applicability of the USEPA's criteria for Korean waters. Since these criteria were prepared with US waters, it is possible that they are not applicable to Korean waters. This study also investigated an effect of enhanced coagulation on particle or turbidity removal. As mentioned earlier, enhanced coagulation aims two targets: particle and NOM removal. Their optimum conditions could be different. The optimum particle removal might aggravate NOM removal, while the optimum NOM removal might aggravate particle removal. Finally, this study attempted to identify the best coagulant for enhanced coagulation.

There are several studies available comparing different coagulants for their effectiveness of NOM removal, but there still remains controversy. Some[5] reported that PACl (poly aluminum chloride) was more effective than alum for enhanced coagulation. Others[6] reported that ferric chloride was consistently more effective than alum in removing NOM. However, these results are not based on the optimum NOM removal, but on the maximum NOM removal.

MATERIALS AND METHODS

One river ("CRW") and two lake waters ("JLW" and "WLW") were used in this study. Since most Korean water treatment plants rely upon surface waters for their raw water sources, river and lake waters were chosen for the study. Of these, "CRW" and "JLW" are currently used as drinking water sources to produce 270,000 m^3/day and 90,000 m^3/day. Water treatment plant using "CRW" relies upon conventional processes of coagulation-flocculation-sedimentation-filtration plus ozonation and GAC adsorption, while the plant using "JLW" relies upon the conventional processes. Characteristics of these three waters are summarized in Table 2. As shown in Table 2, CRW and JLW are low in alkalinity as the most Korean waters. JLW is also low in TOC level, while CRW is relatively high in TOC level. Since WLW has relatively high alkalinity, it is included in the study.

Five different coagulants were used in this study: alum, LAS (liquid aluminum sulfate), PACl, ferric chloride with and without water. These were selected because alum, LAS and PACl are the most commonly used coagulants in Korea. Ferric chloride is included because it is

Table 2. Characteristics of three waters used in this study

	Turbidity, NTU	pH	Alkalinity, mg/L	TOC, mg/L	TDS, mg/L
CRW	1.8~105	6.5~9.0	22~97	3~10	200
JLW	0.7~4.5	6.8~7.2	12~42	1.5~2.6	-
WLW	5.7~20	7.3~8.4	90~110	1.5~10.1	328

known to be effective in NOM removal. Effectiveness of coagulants was evaluated using jar tests. Rapid and slow mixings were conducted at 150 rpm for 1 min and 30 rpm for 20 min. Settling followed slow mixing for 30 min. After settling, supernatant was taken for the analysis of turbidity, pH, TOC, and UV254.

RESULTS AND DISCUSSION

Criteria Applicability

Table 3 summarizes the experimental results of applicability of the USEPA's three criteria for enhanced coagulation on Korean waters. This table shows the results of two waters (CRW and JLW). Two conditions of raw water (LL and ML) were tested for CRW, while only one condition (SLL) was tested for JLW. Since initial TOC level of JLW was mostly less than 2 mg/L, its characteristic was designated as SLL and criterion I (< 2 mg/L) was modified to less than 1 mg/L (criterion I'). The table summarizes whether or not the criteria was satisfied under each condition. Table 3 clearly shows that all of these criteria were achievable for both CRW and JLW. All three criteria were satisfied regardless of coagulant type when CRW was low in TOC and alkalinity levels. The exception was the criterion II (% requirement of TOC removal). According to Table 1, 40 % TOC reduction was required, but it could not be satisfied with alum. As CRW's TOC level became higher (ML), the criterion I (< 2 mg/L) became difficult to achieve. Only Fe-based coagulant was able to satisfy this criterion. However, other criteria (II & III) were easily achieved for all types of coagulant. It was impossible to achieve the new criteria of < 1 mg/L regardless of coagulant type, but other criteria (II & III) were easily achieved for JLW. These results indicate that all of these criteria could be applicable to these waters (CRW and JLW). Use of proper coagulant could satisfy all three criteria.

Controlling criterion means the criterion at which it is satisfied with less coagulant dosage. If criterion I was satisfied at 20 mg/L of coagulant, criterion II at 30 mg/L, and criterion III at 40 mg/L, then criterion I became the controlling criterion. Water treatment plants do not need to satisfy all three criteria. They can select the criterion at which less coagulant is required after testing their waters. Table 4 shows controlling criterion for CRW, JLW, and WLW. Table 4 shows that the controlling criteria can be different depending upon raw water characteristics. When initial TOC level was low,

Table 3. Experimental Results of Applicability of the USEPA's Three Criteria

Type	CRW-LL			CRW-ML			JLW-SLL		
	I[1)]	II	III	I	II	III	I'[2)]	II	III
Alum	S[3)]	NS[4)]	S	NS	S	S	NS	S	S
PACl	S	S	S	NS	S	S	NS	S	S
Fe[5)]	S	S	S	S	S	S	NS	S	S

[1)]I indicates criterion I (< 2 mg/L of TOC); II indicates criterion II (% TOC removal); III indicates criterion III (PODR)
[2)]I' indicates criterion of < 1 mg/L of TOC
[3)]satisfied
[4)]not satisfied
[5)]ferric chloride

Table 4. Controlling criterion for CRW, JLW, and WLW

Initial TOC, mg/L	Initial Alkalinity, mg/L	
	0~60	60~120
< 2	PODR/% removal	-
2~4	PODR/< 2 mg/L	% removal/< 2 mg/L
4~8	% removal/PODR	% removal
> 8	-	% removal

criterion I (< 2 mg/L) could be the controlling criterion. As initial TOC level increased, criterion II rather than I could be the controlling criterion.

An effect of SUVA (specific UV absorbance, UV254/TOC) was then examined. SUVA was known to affect TOC removal.[1] High TOC removal is generally possible for waters with high SUVA values. Therefore, the relationship between the maximum TOC removal and SUVA values as well as initial TOC levels were examined. Figure 1 shows the relationship for initial TOC level, and Figure 2 shows the relationship for SUVA value. Figure 1 clearly shows that initial TOC levels were important for the maximum TOC removal. Higher TOC removal was obtained with the increasing TOC level while initial TOC level was in the range of 1.86~4.86 mg/L, regardless of raw water type. Such tendency was not observed for the SUVA relationship. When SUVA increased from 1.5~2.0 to 2.0~2.5, TOC removal improved, but deteriorated as soon as it increased further to 2.5~3.0. This result justified the use of TOC in TOC-alkalinity matrix. Use of SUVA would not be recommended for preparation of the criterion.

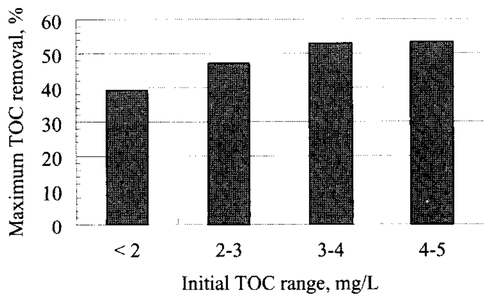

Figure 1. The relationship between the maximum TOC removal and the initial TOC level.

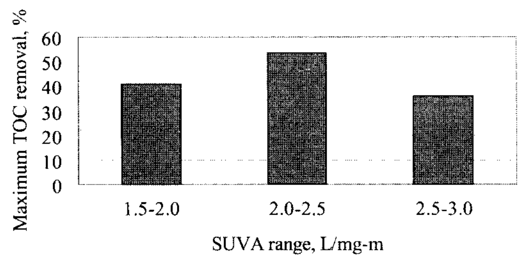

Figure 2. The relationship between the maximum TOC removal and SUVA value.

Conflict between Turbidity and TOC Removals

In order to examine a conflict between turbidity and TOC removals, the minimum coagulant dosages required to satisfy the turbidity criterion and the enhanced coagulation criteria were compared, as shown in Table 5. The turbidity criterion was arbitrarily set to that residual turbidity became less than 1 NTU because it is the typical value obtained after settling. Various raw waters and coagulant types were used for the examination. Turbidity was in the range of 0.7~7.0 NTU and TOC was in the range of 1.86~4.21 mg/L.

Table 5 shows that higher dosage was generally required to satisfy the criteria for enhanced coagulation than the turbidity criterion. However, residual turbidity value was still low at the optimum condition of enhanced coagulation. This result indicates that there was no conflict between turbidity and TOC removals. According to Table 5, residual turbidity was mostly less than 1 NTU at the optimum condition of enhanced coagulation. Here, the optimum condition means the condition at which the minimum coagulant dosage is required to satisfy the controlling criteria. Figure 3, which shows the typical behavior of residual turbidity and TOC/UV254 with increasing LAS dosage, explains the reason why residual turbidity was low at the optimum condition. According to Figure 3, the turbidity criterion was obtained at lower dosage (20 mg/L) than the enhanced coagulation criterion (40 mg/L). The lowest turbidity and TOC levels were obtained with more LAS addition. For this water, 40 mg/L

Table 5. Comparison of Turbidity and TOC Removal

Raw water		Minimum dosage, mg/L			
TOC, mg/L	Turbidity, NTU	Turbidity criterion[1)]	Enhanced Coagulation Criteria: Controlling	Enhanced Coagulation Criteria: II[2)]	Coagulant type
4.21	6.1	20	40 (0.7 NTU)[3)]	40 (0.7 NTU)	LAS
3.17	4.3	30	50 (0.3 NTU)	-[4)]	LAS
3.98	7.0	20	20 (0.8 NTU)	30 (0.6 NTU)	Fe
2.48	1.4	20	20 (0.2 NTU)	60 (0.1 NTU)	PACl
2.04	4.0	10	10 (1.4 NTU)	40 (1.2 NTU)	LAS
1.86	0.7	10	10 (0.1 NTU)	20 (0.1 NTU)	Fe
3.11	10	40	20 (1.3 NTU)	20 (1.3 NTU)	PACl

1)turbidity criterion is residual turbidity less than 1 NTU
2)II means criterion II (% TOC removal)
3)values in parentheses indicate residual turbidities
4)not achieved.

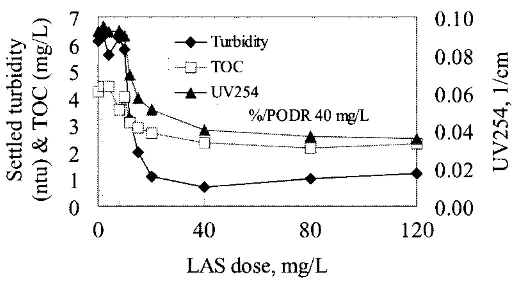

Figure 3. General behavior of residual turbidity and TOC/UV254 with increasing LAS dosage.

was required to reach the lowest turbidity level, which happened to be the optimum condition of enhanced coagulation. Similar results were obtained for other coagulants although they were not shown here.

Best Coagulant for Enhanced Coagulation

TOC removal performances were compared for all coagulants in order to find the best coagulant. These performances were evaluated in terms of both the maximum and the optimum removals. Table 6 compares the maximum TOC removals obtained depending upon coagulant type and raw water. As clearly shown in Table 6, ferric chloride removed more TOC than Al-based coagulants. While the removal was in the range of 36~49% for Al-based coagulants, it was over 60% for ferric chloride for CRW. There was not much difference between the performances of Al-based coagulants (LAS and PACl). TOC removal performance was influenced by raw water characteristics. Such a high removal performance by ferric chloride was not observed for JLW. While Al-based coagulants maintained the similar performances, ferric chloride could not. TOC removal was slightly higher than 40%. These results indicate that ferric chloride is the best coagulant in terms of the maximum TOC removal. However, its effectiveness can be variable depending upon raw water characteristics. Ferric chloride was

Table 6. Maximum TOC Removals Depending upon Coagulant Type and Raw Water

Type	CRW			JLW	
	2~3 mg/L[1)]	3~4 mg/L	4~5 mg/L	1~2 mg/L	2~3 mg/L
LAS	39 (6.58)[2)]	36 (6.80)	49 (6.72)	36 (6.67)	41 (6.68)
PACl	49 (6.48)	40 (6.79)	45 (6.89)	41 (6.49)	-
Fe	60 (6.44)	67 (5.41)	66 (4.94)	42 (6.12)	45 (6.78)

1)initial TOC level of raw water
2)pH value

very effective for CRW, but not for JLW for an unknown reason.

Table 7 compares the minimum dosages required to satisfy the controlling criteria depending upon coagulant type and raw water. Table 8 summarizes the best coagulant for different raw waters, based on the optimum TOC removal. Interestingly, Al-based coagulants were the best coagulant in terms of the optimum TOC removal. Here, the optimum removal means TOC removal enough to satisfy the controlling criteria. Alum or PACl was more effective than ferric chloride, regardless of raw water characteristics when their performances were evaluated in terms of the optimum TOC removal. Even when the evaluation was conducted in terms of criterion II (% requirement of TOC removal), alum or PACl was more effective than ferric chloride. Figure 4 explains why the effectiveness can change depending upon the evaluation tool: maximum or optimum TOC removal. Alum was quick to respond, while ferric chloride was not. As soon as alum was added, TOC level quickly decreased. On the other hand, TOC level started to decrease only after a certain amount of ferric chloride was consumed. Ferric chloride was, however, able to remove TOC in a great extent once the decrease was initiated. Therefore, alum was able to satisfy the controlling criteria at lower dosage than ferric chloride, while ferric chloride could remove more TOC than alum. PACl showed the medium trend between alum and ferric chloride.

Table 8. Best Coagulants for Different Raw Waters Based on the Optimum TOC Removal

Raw water type	Controlling criterion	Criterion II	Raw water
SLL	Alum	Alum	JLW
LL	Alum/PACl	Fe	CRW
ML	-[1]	-	CRW/JLW
MM	PACl	PACl	WLW
HM	Alum	Alum	WLW

[1]no difference was observed

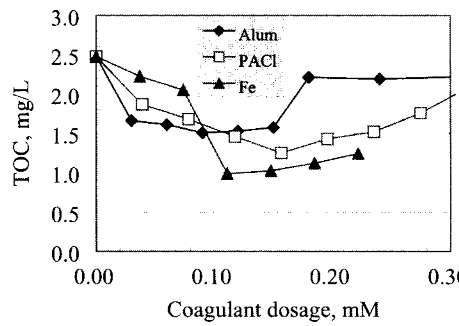

Figure 4. Typical TOC removal for CRW-LL as a function of coagulant dosage.

CONCLUSION

Results of this study showed that all three criteria were achievable for Korean waters of CRW, JLW, and WLW. For these waters, controlling criterion was found to be different depending upon raw water characteristics. When initial TOC level was low (< 4 mg/L), criterion I (< 2mg/L) could be the controlling criterion. As TOC level increased, criterion II (% TOC removal) became the controlling criteria. It was

Table 7. Optimum TOC Removals Depending upon Coagulant Type and Raw Water

Raw water	Type	Initial TOC, mg/L	Minimum dosage, mM		
			LAS/Alum	PACl	Fe
CRW	LL	2~3	0.030	0.039	0.111
		3~4	0.069	0.039	0.074
	ML	4~5	0.055	0.059	0.059
JLW	LL	2~3	0.014	-	0.037
	SLL	1~2	0.030	0.039	0.034
WLW	MM	4~8	0.055	0.020	0.031
	HM	>8	0.027	-	0.037

possible to achieve different goals of turbidity and TOC removals. Although the optimum region of TOC removal was more acidic than that of turbidity removal, there was no conflict between these two removals. The best coagulant was found to be different depending upon the evaluation tool: maximum and optimum removal. Ferric chloride was more effective than alum in terms of the maximum TOC removal, while Al-based coagulant such as alum or PACl was the best coagulant in terms of the optimum TOC removal.

ACKNOWLEDGEMENT

This work was supported by the Kyungnam University Research Fund.

REFERENCE

1. Owens, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G., and Viscosil, K., "NOM characterization and treatability," *J.-Am. Water Works Assoc.*, 87(1), 46-63 (1995).
2. White, M. C., Thompson, J. D., Harrington, G. W., and Singer, P. C., "Evaluating criteria for enhanced coagulation compliance," *J. -Am. Water Works Assoc.*, **89**(5), 64-77 (1997).
3. Black, A. P., Singley, J. E., and Whittle, G. P., "Stoichiometry of the coagulation of color-causing organic compounds with ferric sulfate," *J.-Am. Water Works Assoc.*, **55**(10), 1347-1366 (1963).
4. Ministry of Environment, Korean Drinking Water Standards (2002).
5. Furrey, M. J., Kneser, M., and Henderson, E., "Use of Polyaluminum Chloride and Alum for Enhanced Coagulation at a North Jersey Facility," Proceedings of 25th. WQTC, Denver (1997).
6. Crozes, G., White, P., and Marshall, M., "Enhanced Coagulation: its effect on NOM removal and chemical costs," *J.-Am. Water Works Assoc.*, **87**(1), 78-89 (1995).