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Efficiency of enhanced coagulation for removal of NOM and for adsorbability of NOM on GAC

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ABSTRACT

NOM is known as a precursor to produce disinfection by-products such as THMs and HAAs in drinking water treatment. In this study, NOM removal and THMs reduction were investigated by comparing the conventional coagulation with enhanced coagulation using jar-test. Additionally coagulation efficiency was studied on activated carbon adsorption using adsorption isotherms for natural waters. The experimental data were simulated with IAST to investigate adsorbability of the NOM as multi-components isotherms. The results showed that enhanced coagulation could reduce 10–30% more of DOC and 5–20% more of THMs, respectively, than those of conventional coagulation, Adsorption capacity on activated carbon revealed that the enhanced coagulation had the highest capacity, followed by the conventional coagulation and raw water. The order of adsorption capacity can be explained by increase of strong adsorbable fraction and decrease of initial DOC concentration in enhanced coagulation.

Keywords: GAC; NOM; Adsorption; Enhanced coagulation

1. Introduction

Many problems encountered during water treatment (process) are associated with natural organic matter (NOM). The most critical problem of NOM in the water is a creation of disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) during chlorination. Also, the NOM competes with other synthetic organic carbons (SOCs) for adsorption sites on activated carbon adsorption [1]. Many water treatment utilities need to achieve enhanced coagulation that is defined as a required level of total organic carbon (TOC) removal based on the level of TOC concentration and alkalinity of the source water suggested by USEPA. These rules will also significantly impact other countries' drinking water standard because of growing awareness of the health risk caused by total trihalomethanes (TTHMs) and HAAs. Alternative methods such as chloramination, ozonation or adsorption can be applied to water systems that exceed current or upcoming maximum contaminant levels (MCLs) or include removing disinfection by-products (DBPs) precursors.

NOM removal in drinking water has many advantages such as decreasing the chlorine demand, extending the lifetime for the granular activated carbon (GAC) adsorber, and stabilizing water quality in the distribution system caused by the microbial regrowth. The settled water pH is decreased with adding more coagulants, which can reduce the required concentration x time (CT) value for primary disinfection. When GAC adsorber is used to remove synthetic organics and NOM after the enhanced coagulation and sand filtration certain fraction of NOM can be eliminated by the enhanced coagulation in two ways; one is settling and the other is lowering pH. Extending GAC adsorber bed life is an important

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issue because the GAC adsorber is a relatively expensive treatment process. Optimizing the GAC adsorber can save capital and operation cost. However, applying enhanced coagulation in a conventional water treatment plant can cause some problems such as producing more sludge, which requires a bigger dewatering system than the current system. Also, the optimum turbidity removal may not meet under enhanced coagulation. These problems can be compensated with finished water of a high quality.

In this study, efficiency of enhanced coagulation on GAC adsorption capacity compared to conventional coagulation for NOM and DBP precursors was investigated. The adsorption capacity was evaluated by bottle point isotherm technique and simulated by Ideal Adsorbed Solution Theory (IAST) with Freundlich isotherm. The effect of pH on GAC adsorption was also investigated at the relatively same initial concentration with natural water. Enhanced coagulation was performed by jar-test using poly-aluminum chloride (PACl). Three different water sources from South Korea were used as source water. The NOM removal by enhanced coagulation was compared with conventional coagulation. Finally, the trihalomethanes formation potential (THMFP) was investigated after the conventional and enhanced coagulation.

2. Experimental methods

2.1. Source water

Three water sources were examined in this study. Jamsil reservoir water (JSW) is especially reserved for 14 million people living in Seoul. The characteristics of the source water are summarized in Table 1.

2.2. Batch coagulation

Coagulation, flocculation and sedimentation experiments were conducted at the bench scale using a standard jar-test apparatus with six rectangular 1-L jars. The experiment conditions included 2 min of rapid mixing at 130 rpm, 20 min of slow mixing at 20 rpm and 60 min of sedimentation, respectively. A sampling port located in 3 cm above the bottom in the jar allowed for sample small amount of settled water for analyses. The PACl used in the experiment was 10% of concentrated solution. The actual working solution for coagulation contains 0.31 mg/L of Al^{3+} in 1 mg/L of PACl.

Table 1
Characteristics of source waters

	JSW	PJW	IDW
Turbidity, NTU	5.5–5.6	18–19	1.4–1.5
UV_{254}, cm^{-1}	0.0295	0.044	0.045
TOC, mg/L	1.87	2.20	2.35
Alkalinity as $CaCO_3$ mg/L	22	22	20
pH	7.5	7.2	7.37

2.3. Adsorption isotherm experiments

In order to evaluate the equilibrium GAC adsorption capacity for raw waters, bottle point isotherm methods were performed using different carbon dosages. In this study, F-400 bituminous coal based (Fitrasorb-400, Calgon Corp., Pittsburgh, PA) was used. The GAC was ground through a 100×200 US standard mesh (dp = 0.11 mm). After sieving, the ground carbon was washed with lab clean (LC) water and then decanted until the washed water became clear. Carbon in each bottle was weighed by an analytical balance to ±0.1 mg and placed in a 330 ml amber-colored bottle with Teflon-lined screw caps. Two additional bottles, not containing carbon, were used as controls. The isotherm bottles were placed on tumbler at 20°C for 7 days to help mixing at 13 rpm. After 7 days, samples were taken from each bottle and filtered before analysis using a 50 ml syringe with Millipore HV 0.45 µm pore-diameter membrane.

The experimental data were simulated with ideal adsorbed solution theory proposed by Radke and Prausnitz [2]. This model is usually used to represent the competition adsorption between the fictive components and generate the multicomponent isotherm expression.

2.4. Analytical methods

TOC analysis was performed following method 5310C [3] using TOC analyzer (DC-180) with persulfate/ultraviolet oxidation. Ultraviolet absorbance at 254 nm (UV_{254}) was analyzed using a spectrophotometer (DR-4000). Samples were acidified to pH 2.0 using phosphoric acid for the TOC and the UV_{254} analysis. A quartz cell with a 1cm path length was used, and all readings were corrected for blanks. THMFP was incubated for 168±4 h at 20±1.0°C, buffered at pH 8.0±0.1 with 4 to 1 ratio of chlorine to DOC in order to make sure chlorine is not a limiting factor. THM analysis for all waters was performed with a gas chromatograph (HP-5890) equipped with a purge, trap system and a pursed discharged detector (PDD) using USEPA method 502.2 revision 2.0. The turbidity was measured with a portable turbidimeter (2001A) using method 2140-A.

3. Results and discussion

3.1. Coagulation

Figs. 1 and 2 show settled water TOC data for dosages of PACl ranged from 0.2 to 2.5 mg/L in the various range of pH from 4 to 9 for all three waters. As expected,

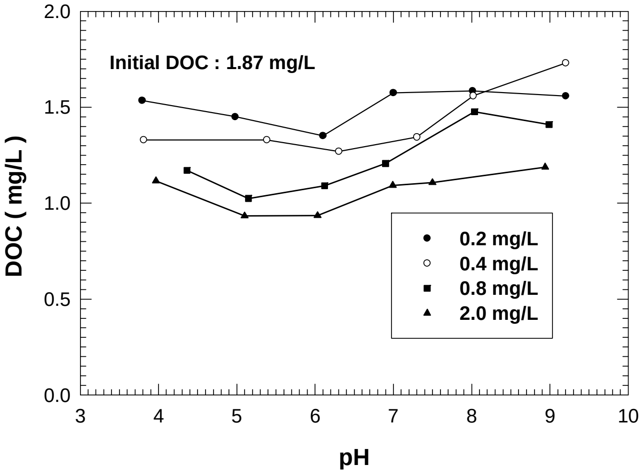

Fig. 1. The effect of pH and PAC dosages on the removal of DOC for JSW.

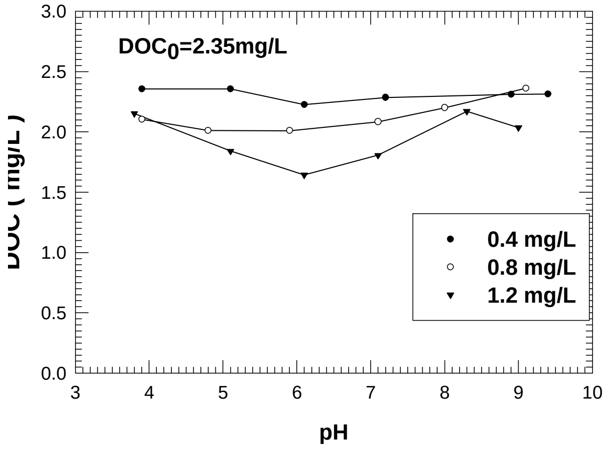

Fig. 2. The effect of pH and PAC dosages on the removal of DOC.

the more PACl added the more TOC removal was observed in all pH range. When the minimum coagulant dosage, 0.2 mg/L of PACl, for turbidity removal was added it showed 0.3 mg/L of TOC removal at pH 6.1 for JSW. This fraction probably corresponds to the particulate and colloidal NOM that could be removed as charge neutralization like other turbidity causing compounds. However, no significant TOC removal was observed with 0.4 mg/L of PACl for IDW at all pH. As the coagulant dosages were increased the removal of NOM was significantly improved for all waters. This fraction of NOM is removed by the mechanism of coprecipitation by adsorption of the NOM on the metal hydroxide. As shown in Fig. 1, for JSW, the TOC concentration was decreased from 1.35 to 0.91 mg/L with increasing the coagulant dosage from 0.2 to 2.0 mg/L at similar pH value, respectively. Fig. 2 shows the results of TOC removal for IDW. The TOC concentration was decreased from 2.25 to 1.6 mg/L with increasing the coagulant dosage from 0.4 to 1.2 mg/L at pH 6.1, respectively.

As shown in Table 2, turbidity of treated waters was not significantly improved after enhanced coagulation compared to the conventional coagulation. Compared with conventional coagulation, enhanced coagulation significantly increased TOC and UV_{254} removal especially for IDW as shown in Fig. 4. Removal of TOC and UV_{254} was increased by 5–30% for all waters. According to the jar-tests, excessive coagulants cannot help to increase the NOM removal more than the samples obtained in enhanced coagulation for each water. Many researchers reported that hydrophilic compounds of NOM and low molecular weight compounds are hardly removed by coagulation. Therefore, the removal of TOC can be varied from water to water depending on the chemical or physical composition and origin of NOM. PJW showed the lowest TOC and UV_{254} removal percentage. The water may contain more hydrophilic fraction or less molecular weight fraction, which can hinder the coagulation.

3.2. DBP formation

Fig. 3 shows the results of THMFP data after conventional and enhanced coagulation. THMFP can be reduced by conventional coagulation as much as 37% for PJW. Generally, THMFP reductions for all waters were much higher after enhanced coagulation by decreasing initial DOC concentration or selective removal of DBP precursor. Even though the removal percentage of THMFP was lower than that of TOC in the enhanced coagulation, the difference of removal percentage of THMFP was much

Table 2
Summary of treated water quality after coagulation

	Jamsil water (JSW)		Indeokwon water (IDW)		Paju water (PJW)	
	Conventional	Enhanced	Conventional	Enhanced	Conventional	Enhanced
PACl, mg/L	0.8	2.0	0.6	1.2	1.5	2.5
TOC removal, %	41.4	50.2	5.50	30.2	41.5	52.7
pH	6.1	6.0	6.1	6.1	6.5	5.7
Turbidity, NTU	0.3	0.2	0.3	0.1	0.3	0.3

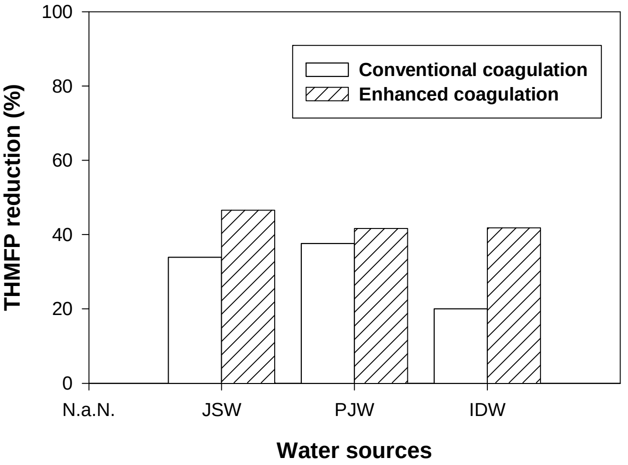

Fig. 3. The comparison of THMFP reduction of conventional coagulation and enhanced coagulation.

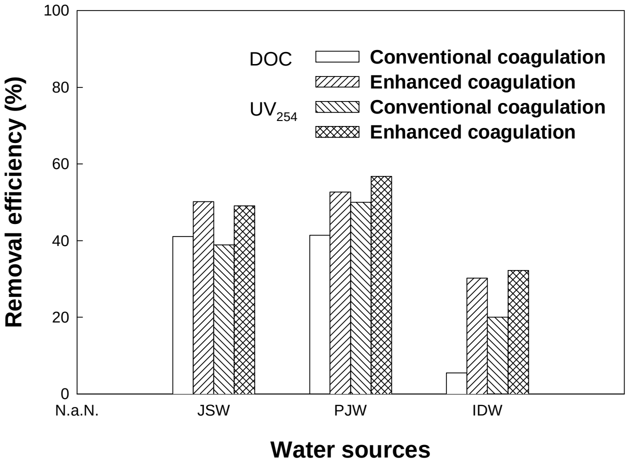

Fig. 4. The comparison of DOC and UV_{254} removal of conventional coagulation and enhanced coagulation.

higher than that of TOC "in the conventional coagulation compared with enhanced coagulation." This indicates selective DBP precursor removal by enhanced coagulation. The THMFP yield was decreased by an average of 43%; ranged from 41 to 47%, after enhanced coagulation. The THMFP of unit TOC concentration was varied from 63 to 77 µg/mg TOC because of different characteristics of NOM caused by different origins and chemical structures. If utilities cannot meet the DBP regulations by enhanced coagulation because of complexity of NOM they have to adapt the advanced treatment process such as GAC adsorption membrane to eliminate more DBP precursors.

3.3 Adsorption isotherms

The Freundlich *K* values and fictive component concentrations for the three waters examined are shown

Table 3
Comparison of fictive components for JSW

Raw water, DOC0= 1.66 mg/L, pH = 7.5, APE = 5.57 %				
K values	0	5	25	60
$C_{i,0}$ (%)	11.76	9.06	10.71	68.48
Conventional coagulation, DOC0 = 1.25 mg/L, pH = 6.1, APE = 4.43%				
K values	0	5	25	60
$C_{i,0}$ (%)	10.75	4.64	24.0	60.54
Enhanced coagulation, DOC0 = 1.02 mg/L, pH = 6.0, APE = 3.96 %				
K values	0	10	25	90
$C_{i,0}$ (%)	13.96	2.90	2.89	80.25

Table 4
Comparison of fictive components for IDW

Raw water, DOC0= 2.15 mg/L, pH = 7.3, APE = 3.75%				
K values	0	10	25	70
$C_{i,0}$ (%)	15.8	7.28	24.2	52.73
Conventional coagulation, DOC0 = 1.94 mg/L, pH = 6.1, APE = 4.38%				
$C_{i,0}$ (%)	11.77	12.59	17.24	58.39
Enhanced coagulation, DOC0 = 1.41 mg/L, pH = 6.1, APE = 2.08%				
$C_{i,0}$ (%)	15.6	4.91	5.75	73.7

Table 5
Comparison of fictive components for PJW

Raw water, DOC$_0$= 1.36 mg/L, pH = 7.1, APE = 3.86%				
K values	0	10	25	50
$C_{i,0}$ (%)	16.29	29.43	34.03	20.25
Conventional coagulation, DOC$_0$ = 1.00 mg/L, pH = 6.5, APE = 3.65%				
$C_{i,0}$ (%)	11.31	1.69	23.15	63.84
Enhanced coagulation, DOC$_0$ = 0.91 mg/L, pH = 5.7, APE = 3.86%				
$C_{i,0}$ (%)	11.10	4.73	0.00	84.17

Tables 3, 4 and 5. Table 3 shows the adsorption isotherm results that compare these three water sources for JSW before (raw water) and after conventional and enhanced coagulation, respectively. The lowest *K* values were varied from 5 to 10, mid- *K* value was fixed at 25 and the highest *K* values were varied from 60 to 90. The non-adsorbable fraction concentration was relatively constant before and after coagulation. However, the mid-adsorbable fraction was increased from 10.70 to 24.07% after conventional coagulation, which resulted from decreasing the initial concentration and pH value. After enhanced coagulation, the strong adsorbable fraction was significantly increased from 60.54 to 80.25%, which was shifted from the weakly and mid-adsorbable fraction. The highest K value was also increased from 60 to 90 because the experimental data after enhanced coagulation could not be fitted to Freundlich *K* value at 60.

Table 4 compares adsorption isotherm before and after coagulation. The *K* values for each fictive component were fixed at 10, 25 and 70 as a weakly, mid and strong adsorbable fraction, respectively. As shown by results, the DOC concentration of non-adsorbable fraction was decreased from 0.34 to 0.2 mg/L after coagulation without significant changes in percentage. After conventional coagulation, the concentration of mid adsorbable fraction was slightly decreased while the strong adsorbable fraction stayed in constant. However, the percentage of strong adsorbable fraction was increased from 52.7 to 58.4% because of decreasing initial DOC concentration. After enhanced coagulation, the percentage of strong adsorbable fraction was significantly increased from 52.5 to 73.7% compared to before coagulation. Also, weakly and mid adsorbable fraction was hardly detected.

Table 5 shows the results for PJW. The K values for each fictive component were fixed at 10, 25 and 50 for weakly, mid and strong adsorbable fraction, respectively. The DOC concentration of non-adsorbable fraction was decreased from 0.22 to 0.1 mg/L after coagulation. Same as other two waters, the strong adsorbable fraction was significantly increased after enhanced coagulation.

The roles of enhanced coagulation are to reduce the initial concentration, and to decrease the pH value and selective removal of large molecular weight NOM or DBP precursors. If only hydrophobic compounds were removed in the enhanced coagulation, this may negatively affect the adsorption on GAC because GAC can preferentially adsorb hydrophobic compounds rather than hydrophilic compounds. If this is true, only reasons to improve the adsorbability of NOM on GAC are decreasing initial concentration and pH value. Otherwise the adsorption capacity of NOM should be decreased. As shown in Tables 3–5, the strongly adsorbable fractions were significantly increased, which is more than the effect of initial concentration and pH value. This improvement of adsorbability cannot be occurred without changing characteristics of NOM because certain amounts of hydrophobic compounds were removed in the enhanced coagulation,that impose containing more hydrophilic compounds after enhanced coagulation

4. Conclusions

In this study, the bench-scale experiments evaluating enhanced coagulation with PACl showed that using maximum three times more coagulants performed superior TOC removal without significant turbidity removal for all three water. The optimum pH values for TOC removal by enhanced coagulation were around 6.0. The excessive coagulants cannot help to increase the DOC and UV_{254} removal more than obtained in the enhanced coagulation for all waters. Among the three waters, DOC removal obtained after enhanced coagulation was 50.2%, 30.2% and 52.7% for JSW, IDW and PJW, respectively. THMFP could be reduced by conventional coagulation as much as 37% for PJW. The difference of removal percentage of THMFP was much higher than that of TOC in conventional coagulation compared with enhanced coagulation. The DOC was divided into a non-adsorbable fraction and three fictive adsorbable fractions. After enhanced coagulation, the strong adsorbable fraction was increased by 20% with the highest K value from 60 to 90 for JSW. Other two waters showed the same percentage increase of strong adsorbable fraction with decrease of weakly and mid adsorbable fractions. Also, the pH impact was investigated on adsorption isotherm of DOC. The adsorbability of the DOC was increased with decreasing pH for untreated water and after conventional coagulation. An increase to pH 8.6 resulted in an increase in the mid adsorbable fraction from 5.5 to 38.0% and in the weakly adsorbable fraction from 2.2 to 5.7% and decrease in the strong adsorbable fraction 80.4 to 42.1% for the water after conventional coagulation.

Acknowlegement

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