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EFFECT OF PREOZONATION IN DRINKING WATER TREATMENT USING POLYAMINE FLOCCULANT

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Abstract : The effects of preozonation and synthetic polyamine flocculant on the removal of turbidity, TOC (total organic carbon) and UV_{254} in drinking water treatment were investigated. The preozonation was tested using two treatments: i) conventional treatment using inorganic coagulant alone, ii) improved coagulation using the polyamine flocculants in combination with inorganic coagulant. The effects of ozone concentration, contact time and polymer dosage on the removal of organic compounds were investigated via both jar and pilot tests. Preozonation significantly increased the removal of turbidity, TOC and UV_{254} at all treatment levels investigated (1, 2 mg/L for ozone, and 0.3~1.5 mg/L for polyamine flocculant). The optimum ozone concentration and polymer flocculant dose were about 1 mg/L (ozone contact time: 10 min) and 0.8 mg/L, respectively. The results of laboratory and pilot-plant studies indicate that preozonation has a synergistic effect on the removal of turbidity, TOC and UV_{254} in Nak-Dong river water treatment using a polyamine flocculant.

Key Words : polyamine flocculant, preozonation, TOC, turbidity, UV_{254}

INTRODUCTION

Surface water, used as a source of tap water, usually contains natural organic matters (NOMs). The NOMs often produces disinfection byproducts (DBPs) during the disinfection processes. Therefore it is important to develop a technique to remove organic matters effectively to minimize the DBP formation. In the most of source water (river and lake) used drinking water, seasonally excess growth of algae causes taste and odor and adverse effect on coagulation/sedimentation process leading short backwash time at filtration process by fouling of filter. Consequently water production reduced. The most of water treatment plants (WTPs) has introduced pre-chlorination for the purpose of solving those problems. For a long time, the so-called break point chlorination was the first treatment step before coagulation to oxidize ammonia and to disinfect the water. However, the process produce disinfection by-products, such as trihalomethanes (THMs) and holoacetic acids (HAAs).[1,2]

For the removal of organic matters such as precusors (NOMs) of DBPs within source water, pre-chlorination has been used as preoxidant. However, subsequently the formation

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of DBPs increased and the coagulation in the following process may be deteriorated, as well as less effective at high pH and low temperature.[3,4)]

Moreover, during a period of heavy rain in summer the water containing high turbidity, may be resalted in a high residual aluminum concentration as high dose of inorganic coagulants. Addition of small amounts of polyamine flocculants with reduced inorganic coagulant increased the coagulation efficiency and reduced residual aluminum in our laboratory experiments for pre-chlorination water.[5,6)] Also, polyamine flocculant can also achieve effective removal of algae.[7)]

Recently, ozonation have been considered as alternative process for removal of NOM and effectively disinfection.[8,9)] Some WTPs have employed the ozone process as disinfection and many WTPs are being considering the process. It is very important to understand its effects on coagulation in general and on organic matter removal in particular. The effect of ozone on coagulation was found to depending on the characteristics of raw water quality.[10~12)]

In this study, preozonation and polyamine flocculant synthesized in our laboratory were tested for drinking water treatment. Preozonation and synthesized polyamine flocculant were applied to the Nak-Dong river water in Korea to examine their efficiency on the removal of turbidity, TOC and UV_{254}.

MATERIAL AND METHODS

Polyamine Synthesis

Polyamine flocculants were synthesized in a 2 L glass reactor equipped with temperature controller and mechanical stirrer. Polyamine flocculants were synthesized by two-step polycondensation of dimethylamine (DMA) and epichlorohydrin (EPI).[13,14)] In the first step, epichlorohydrin (0.98 mole) was reacted with mixture (1.0 mole) of dimethylamine and modifying agent by adding dropwise through a dropping funnel for 3~5 hours at 25~40℃ to form oligomers. In the second step, polycondensation was conducted by stirring for 2~5 hours at 70~95℃. After reaction completed, aqueous polyamine solution was diluted with deionized water (DI water≥16 MΩ) to obtain 50% (wt%) solid content. The molecular weight of the obtained polymer was determined by intrinsic viscosity. The intrinsic viscosity, $[\eta]$, of polymer product was 0.065 (AQfloc) that corresponds to approximately 13,000 g/mol (Table 1).

PAC (polyaluminum chloride, Al_2O_3 = 17 wt%) and the synthesized polymer flocculant were used in this study.

Raw Water Quality

Raw water quality in water treatment plant was observed as follows: turbidity (7~13 NTU), TOC (3~6 mg/L), UV_{254} (0.06~0.11 cm^{-1}), alkalinity (38~43 mg/L as $CaCO_3$) and pH (7.8~8.3). That was the result of water analysis, which was observed during the last 6 months back to the winter.

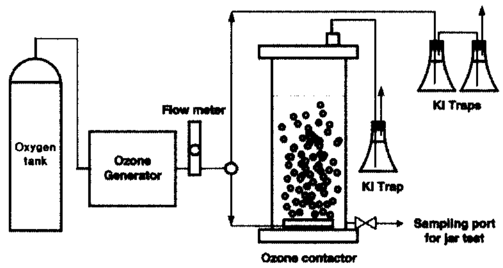
Preozonation

Ozone contactor in bench-scale was equipped a 30 L water column with contact volume size of 20 L (Figure 1(a)). Ozone generator (HD-

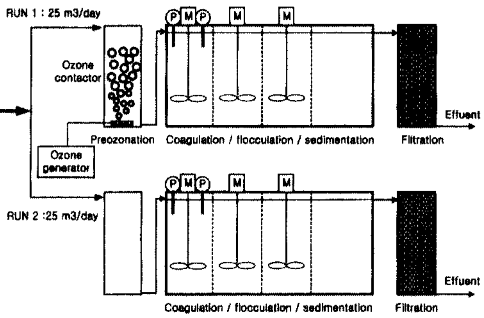
Table 1. The characteristics of polyamine flocculant

		MCLs** by Korea	MCLs by AWWA	AQFLOC	Superfloc 567C***
Intrinsic viscosity η (dL/g)		-	-	0.065	0.052
M.W.* (g/mol)		-	-	13,000	10,000
Residue concentration (ppm)	EPI	20	20	0.03	0.99
	DCIPA	Total 2,000	1,000	3.13	2.52
	DCP		1,000	47.29	13.32
	CPDO		1,000	0.05	0.40

*estimated by mark-houwink-sakurada equation,[15)] **maximum contaminant level, ***commercial polyamine



(a) Bench-scale



(b) Pilot-plant

Figure 1. Schematic of (a) bench-scale ozone contactor and (b) pilot plant.

400, Ho-Dong electrical Co, Daegu, Korea) producing 0.4 g O_3/hr was used. Preozonation was conducted with variable ozone concentration and 5, 10 and 20 min of contact time to find out the effects of ozone dose and contact time.

Ozone generator (Trailigaz Co, France) for pilot plant, introduced the ozonated air to the bottom of the column through a diffuser (Figure 1(b)). The ozone was produced from dried air at a rate of 22 g ozone/m^3 air at an air flow rate of 0.15 L/s. Hydraulic retention time (HRT) in the ozone contactor was about 8.2 min and adjusted ozone dose concentration by control valve.

The ozone concentration was determined by Indigo colorimetric method[16] in bench-scale preozonations and by ozone analyzer (BMT MessTechnik, BERLIN, Germany) in pilot-scale experiments.

Jar Test

A jar-tester (Phipps & Bird Stirrer, Model 7790-400) equipped with six-paddles was used for the laboratory experiment tests. For the jar test, 1-L of ozonated or non-ozonated water sample was transferred into each jar. Coagulants used in this research were PAC and polyamine polymer, which was synthesized in our laboratory. The desired amount of inorganic coagulant and/or polymer was added to each jar first while mixing rapidly at 350 rpm for one minute to simulate rapid mixing. The speed was reduced to 60 rpm for 15 min and 30 rpm for 5 min to provide flocculation. The paddles then were removed and the contents of each jar were allowed to settle quiescently for 60 min (Table 2(a)). After settling, 50 mL sample of the settled water was taken carefully just below the water surface using a sampling port. Turbidity (Hach turbidimeter, Model 9200 N) was measured immediately. TOC was determined by TOC analyzer (Shimadzu, TOC-5000A). UV_{254} was also determined to observe the removal of humic substances in the water. The samples were filtered through a 47 mm cellulose nitrate filter (0.45 μm) and measured by UV absorbance at 254 nm using UV-VIS spectrophotometer (Hewlett Packard, Model 8452A).

Table 2. The operating conditions of jar test and pilot test

(a) jar-test

Sample volume	1 L
Rapid mixing - time	350 rpm - 1 min
Slow mixing step 1 - time	60 rpm - 15 min
Slow mixing step 2 - time	30 rpm - 5 min
Sedimentation time	60 min

(b) pilot-test

Flow rate	25 m^3/day
Preozonation contact time	8.2 min
Rapid mixing	120 rpm
Slow mixing step 1	12 rpm
Slow mixing step 2	9 rpm
Sedimentation time	230 min
Sand filteration time	10 min

Pilot-test

Optimum conditions obtained from the result in bench-scale test were applied to pilot-scale one. Pilot test was designed to compare two different conditions (preozonation and non-ozonation) at a time with water treatment volume of 25 m^3/day (Figure 1(b)). The operating conditions of the pilot plant system are summarized in Table 2(b). After each experiment 200 mL of effluent was taken out and turbidity was measured immediately. TOC and UV_{254} were also determined to observe the removal of organic matters in the water by preozonation and polyamine flocculant. The consumption of $KMnO_4$ was measured to quantify easily oxidizable matters.

RESULTS AND DISCUSSION

Jar Test

Effect of preozonation : In bench-scale preozonation, the effect of contact time on turbidity, TOC and UV_{254} removal of ozonated water were investigated. Jar tests were conducted on ozonated waters with variable contact time (0~20 min). The result of jar test on the ozonated water with the different contact time obtained the optimum PAC dosage of 30 mg/L. Figure 2 shows turbidity, TOC and UV_{254} removal on the preozonation contact time at a fixed PAC dosage (30 mg/L). As contact time increasing, the removal efficiency increased. At a fixed ozone concentration (0.88 mg/L), the optimum contact time is found to 10 min. However, longer contact time (20 min) decreased turbidity and TOC removal. Particles and organic matters in raw water may be deteriorated of coagulation process due to production of smaller molecular organic matters and ozonation byproducts.[17)]

Effect of polyamine concentration : Figure 3 shows the effect of the polyamine flocculant dosage on turbidity, TOC and UV_{254} removal at fixed ozone dose (1.0 mg/L) and contact time (10 min). With a fixed amount of PAC (15 mg/L), the effect of polyamine flocculant

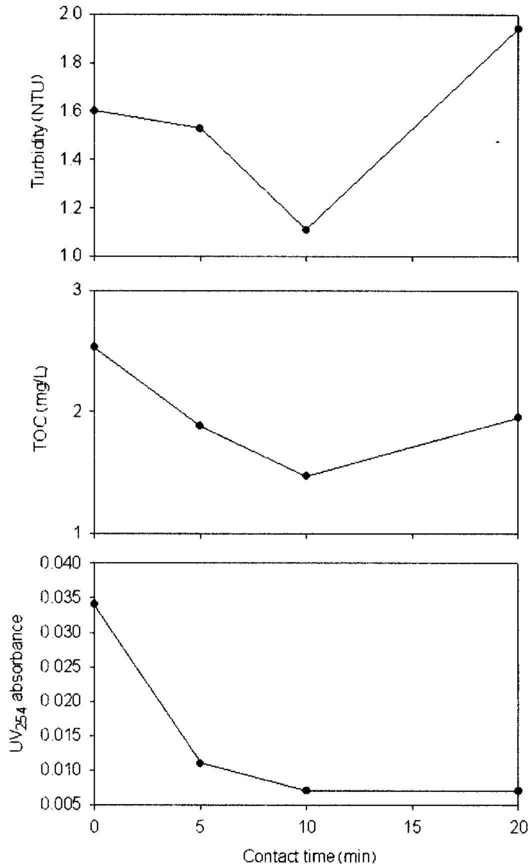


Figure 2. Effects of contact time on the removal of Turbidity, TOC and UV_{254} (optimum PAC dosage 30 mg/L, ozone concentration 0.88 mg/L, raw water turbidity 25 NTU, TOC 5.3 mg/L, UV_{254} 0.078 cm^{-1}).

dosage was investigated. When the concentration of polyaimine flocculant is less than the optimum dosage (0.6 mg/L), the turbidity decreased sharply, however, beyond this optimum value tends to remain almost constant. The most effective removal of turbidity, TOC and UV_{254} is obtained when sufficient polyamine flocculant adsorbed on the surface of metal precipitates. Inorganic coagulants and polyamine flocculant in combination system, a suitably preozonation (concentration and contact time) has positive effect for the removal of organic compounds.

If there is excessive organic polymer, it may

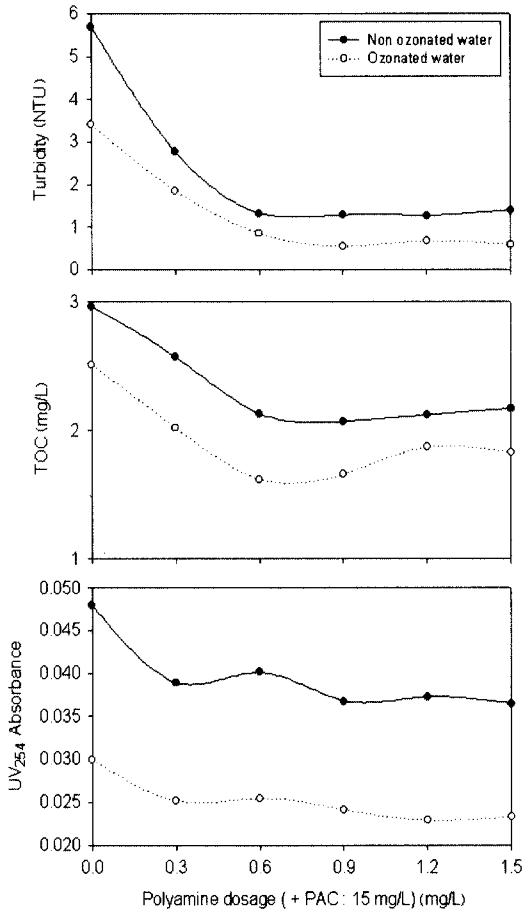


Figure 3. Effect of polyamine dosage on w/ and w/o preozonation (raw water: turbidity 24 NTU, TOC 4.3 mg/L, UV_{254} 0.083 cm^{-1}).

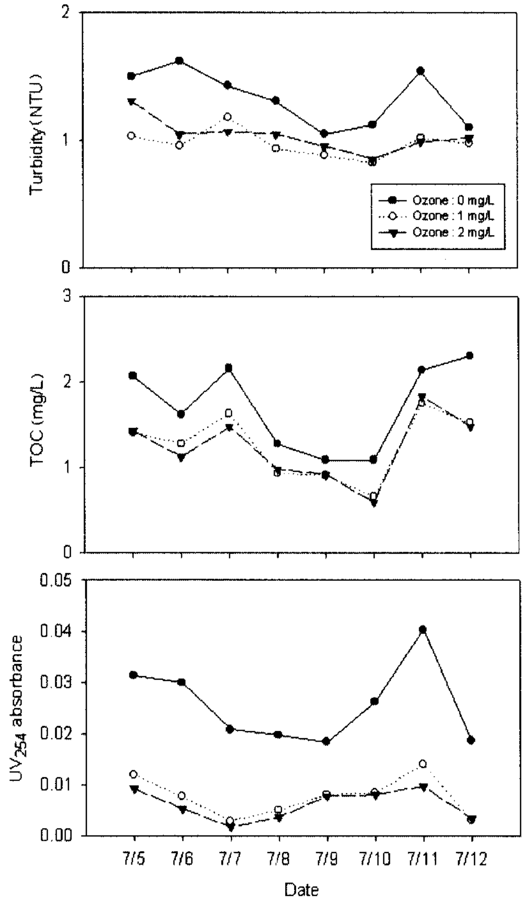


Figure 4. Effects of ozone dose on the removal of turbidity, TOC and UV_{254} in pilot-plant.

cause a second polymer adsorption on the top of the primary adsorption layer, presumably forming a surface that inhibits the attachment of metal precipitates. The presence of a polyamine flocculant overdose makes the floc less settleable.

Pilot Test

Effect of ozone concentration : Figure 4 shows the effect of ozone dosage on the removal of turbidity, TOC and UV_{254} at a fixed contact time (8.2 min). Preozonation to raw water lowered the TOC by a small amount (about 15%). However, preozonation of the raw water significantly destroyed the UV measured at 254 nm (about 50%) partly as a result of the effects of preozonation on humic substances containing aromatic groups and double bonds. The optimal ozone concentration was obtained at the range of 1.0 mg/L, while 2.0 mg/L of ozone increase the turbidity by the same mechanism explained in the results of jar test.

Effect of polyamine flocculant : Effect of polyamine flocculant on the removal of turbidity, TOC and UV_{254} was examined. Water samples with low turbidity (Table 3) and high turbidity (Table 4) were tested and compared. In Table 3, application of 12 mg/L of PAC lowered the turbidity below 1.30 NTU. At

Table 3. Effect of polyamine flocculant on the removal of turbidity, TOC and UV_{254} at low turbidity in pilot test

Raw water quality			Flocculant(mg/L)		Sedimentation			Sand filtration		
Turbidity (NTU)	TOC (mg/L)	UV_{254} (cm^{-1})	PAC	Polyamine polymer	Turbidity (NTU)	TOC (mg/L)	UV_{254} (cm^{-1})	Turbidity (NTU)	TOC (mg/L)	UV_{254} (cm^{-1})
5.82	3.42	0.074	12.0	0	1.30	1.97	0.057	0.54	1.52	0.036
			7.5	0	2.22	2.53	0.072	1.27	2.01	0.047
			7.5	0.4	1.17	1.95	0.055	0.52	1.38	0.033

Table 4. Effect of polyamine flocculant on the removal of turbidity, TOC and $KMnO_4$ at high turbidity in pilot test

Raw water quality			Flocculant(mg/L)		Sedimentation			Sand filtration		
Turbidity (NTU)	$KMnO_4$ (mg/L)	UV_{254} (cm^{-1})	PAC	Polyamine polymer	Turbidity (NTU)	$KMnO_4$ (mg/L)	UV_{254} (cm^{-1})	Turbidity (NTU)	$KMnO_4$ (mg/L)	UV_{254} (cm^{-1})
125	22.3	0.865	72	0	2.00	3.9	0.103	0.09	3.2	0.086
			48	0	5.50	4.8	0.154	2.22	3.9	0.125
			48	0.8	2.30	3.8	0.106	0.10	3.2	0.086

Table 5. The effect of polyamine concentration on the removal of turbidity, TOC and UV_{254} in pilot test

Raw water quality			Flocculant(mg/L)		Sedimentation			Sand filtration		
Turbidity (NTU)	TOC (mg/L)	UV_{254} (cm^{-1})	PAC	Polyamine polymer	Turbidity (NTU)	TOC (mg/L)	UV_{254} (cm^{-1})	Turbidity (NTU)	TOC (mg/L)	UV_{254} (cm^{-1})
5.57	3.14	0.073	12.0	0	1.10	1.97	0.057	0.24	1.52	0.029
			12.0	0.4	0.87	1.75	0.040	0.22	1.38	0.021
			12.0	0.8	0.43	1.41	0.033	0.18	1.23	0.019

lower concentration of PAC (7.5 mg/L), removal efficiency of turbidity, TOC and UV_{254} was highly improved by addition of small amount (0.4 mg/L) of polyamine flocculant. The polyamine flocculant was also tested water samples of high turbidity by rainfall (Table 4). This was carried out to see if polyamine flocculant can be used to treat raw water with high turbidity. High fluctuation in turbidity is often observed in the Nak-Dong river water due to heavy rain in summer. For the treatment of raw water containing 125 NTU, addition of high concentration of PAC (72 mg/L) lowered the turbidity to below 2.0 NTU. This can be improved by adding small amount (0.8 mg/L) of polyamine flocculant. At a fixed amount (48 mg/L) of PAC, addition of 0.8 mg/L of polyamine efficiently lowered turbidity, TOC and $KMnO_4$ consumption. The addition of 0.8 mg/L of polyamine flocculant reduced 33% of PAC consumption. This result is similar to that of jar-test.

Table 5 shows the effects of the polyamine dosage on turbidity, TOC and UV_{254} removal at an average turbidity of 5.57 NTU. The polyamine concentration was varied to determine optimal polyamine concentration at constant amount of PAC (12 mg/L). 12 mg/L of PAC was not able to reduce the turbidity to below 1 NTU, but turbidity, TOC and UV_{254} removal were highly improved by adding 0.4～0.8 mg/L of polyamine flocculant. Both 0.4 mg/L and 0.8 mg/L successfully lowered the turbidity below 1 NTU. This suggests that addition of small amount of polyamine flocculant can highly improve drinking water

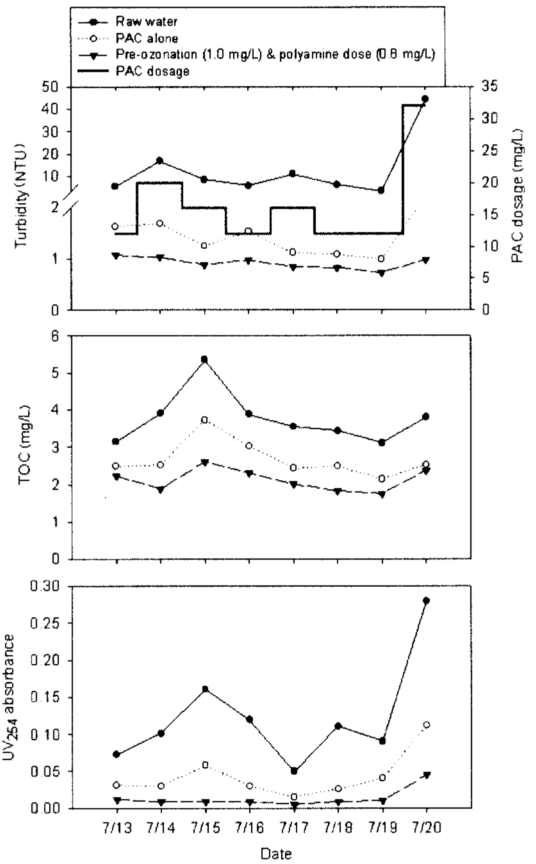


Figure 5. Comparison of the effects between conventional and improved water treatment in pilot-test.

quality by means of reducing 12% of turbidity and 15% of UV_{254}.

Effect of improved water treatment : Figure 5 shows the improvement of flocculation efficiency using PAC, 0.8 mg/L of polyamine flocculant and 1 mg/L of preozonation compared with that of conventional water treatment adapting only PAC. The use of preozonation and polyamine flocculant in conventional water treatment can improve about 30% flocculation efficiency on the removal of turbidity and UV_{254}. In the pilot test conducted in summer to clarify the difference of removal efficiency between conventional water treatment and improved water treatment, the removal rate of turbidity, TOC and UV_{254} increased, which was ranged from 10~15, 15~25 and 30~60% respectively.

CONCLUSIONS

Improvement of flocculation efficiency by preozonation and polyamine flocculant in drinking water treatment was investigated and the results are summarized as follows.

1. Preozonation significantly increased the removal of turbidity, TOC and UV_{254} at all treatment levels investigated with the optimum ozone dose about 1.0 mg/L (at contact time 10 min) in this work.
2. Polyamine polymer was used to improve flocculation efficiency in coagulation process. In jar and pilot test, the addition of polyamine flocculants brought a reduction of 30~40% in the consumption of inorganic flocculant. It can also be used to reduce the amount of coagulant subsequently to reduce the amount of sludge and the optimum concentrations of polyamine flocculant were 0.6~0.8 mg/L in this study.

This study reveals that the use of preozonation and polyamine flocculant in conventional water treatment can improve about 30% flocculation efficiency. These results indicate that organic matters can be effectively removed by preozonation and small amount of polyamine flocculant addition in drinking water treatment.

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