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Pilot Scale Assessment of DOC and THMs Removal in Conventional Water Treatment System

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This research aims to investigate the behavior of organic matter that causes bacterial re-growth and the formation of disinfectant by-products such as THM in water treatment, and to optimize conditions for a more efficient and conventional water facility. THM removed 51 % and 12 % through coagulation/sedimentation and filtration using a selected conventional system. In this experiment, the removal ratio of DOC was highest at 68 % when the Gt value was 42,000 and lowest at 41 % when the Gt value was 30,000. 77-84 % of total DOC was removed during coagulation/sedimentation, and 15-23 % was removed during filtration. When Gt values were between 30,000 and 66,000, over 50 % of high molecular matter above 10 K during coagulation/sedimentation was removed. Turbidity removed 98 % when the Gt value was 66,000. As the Gt value increased, the turbidity removal ratio increased. Turbidity removed over 20 % during the filtration process.

Key Words : DOC, THM, Molecular Weight Distribution, Gt.

1. Introduction

The purpose of water treatment is to produce safe, sanitary, and astatically respectable water with inactive microorganisms in order to minimize the use of harmful disinfection by-products during water treatment. The formation of by-products share characteristics with organics in the water treatment processes[1].

The process of removing natural organic material includes enhanced coagulation, absorption, ozone oxidation, pre-chlorination, and membrane separation[2,3]. 30-50 % of dissolved organic carbon was removed through a conventional water system[4]. Organics in the range of MW 100-3,000 were removed after coagulation/sedimentation when Nacdong river was used as a raw water[5]. Veenstra et al (1985) reported that organic carbon material over MW 5,000 was removed using alum and polymer.

The introduction of additional processes such as ozone and biological activated carbon processes are being promoted in order to reduce disinfectant by-products and precursors[6]. However, before the introduction of an advanced water purification process, existing processes must be improved and optimized[7].

UV absorbance at 254 nm can be used in the estimation of organic matter because it has a linear relationship with the concentration of carbon[8,9]. Traina et al reported humic acid has a close correlation with UV absorbance at 272 nm. Bartels showed DOC in the sedimentation layer has a linear relationship with TOC and UV absorbance at 254 nm. Eaton (1995) reported UV absorbance at 254 nm indicating lignin, tannin, humic matter, and saturated compounds[10]. When the SUVA value is between 4 to 5, it means organics are relatively hydrophobic, aromatic, and of high molecular weight compared to water with lower SUVA values[11].

It has been reported that disinfectant byproducts such as THM are carcinogenic. They are formed during water chlorination with organics[12,13]. These organics could be the cause of re-growth in water distribution systems and tanks. DBP form quickly at a distribution of under MW 300 and compose 50 % of the formation of THM.

This research aimed to investigate characteristic variations of organic matter after water treatment when

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Han River was used as a raw water in a pilot scale, and to understand the removal ratio of THM under the same conditions for the selection and modification of a water process to minimize DBP. Another purpose for this research was to analyze the interrelationship between DOC in each process and THM in a conventional water system.

2. Materials and Methods

2.1. Operation of pilot plant

The equipment for this research was composed of a grit chamber, chlorine contactor, coagulation, sedimentation and filtration systems. The pilot scale system for this research is illustrated in Fig. 1. Raw water stayed in the grit chamber for 10-20 min at a 3-4 effective depth. The chlorine contactor was of rectangular shape with a width of 0.5 m, height 2.3 m, and length 1.4 m. 2-3 mg/L of chlorine was added which allowed the residual chlorine to be approximately 0.1-0.2 mg/L at coagulation.

Poly aluminum chloride was used as a coagulant, and input concentration was selected by using a Jar test according to the turbidity change in the water. The basin for rapid mixing had a width of 0.6 m, length 0.6 m, height 0.9 m, and composed of a vaned disk with four flat blades. The basin for slow mixing had a horizontal paddle, and G value was controlled from 10 and 75 sec. Retention time at the basin for rapid and slow mixing was 1 and 20 min. The sedimentation basin had a width of 1.2 m, length 7.5 m, height 1.7 m, retention time was 3.5 hr, and two basins were operated for sedimentation.

A sand filter facility consisting of two rooms for filtration at a width of 0.6 m, length 0.55 m, height 2.3 m, and 70 cm of sand media with an effective diameter between 0.45- 1 mm. It operated 150 m/day. Back washing of the filtered sand was adjusted to start automatically depending on the head loss during filtration. Back washing time consisted of water at 3 min, air 2.5 min, air and water together at 2.5 min, water 2.5 min, and water drainage at 3 min for a total program of 13.5 min.

2.2. Monitored parameters

The experimental water process at the plant was brought from the Han River provided by a water facility in Incheon. 100 tons of water was taken in daily. The samples consisted of water requiring an analysis of water temperature, pH, turbidity, head loss, UV_{254}, UV_{220}, DOC, and THM.

Turbidity was measured with an HACH Model 2100A (HACH, USA). Samples for UV_{254} and UV_{220} were filtered through a pore size of 0.45 μm PVDF(Polyvinylidene Fuloride). Then, absorbance was measured at a wavelength of 220, 254 nm using a UV-visible spectrophotometer (UV-1601, Shimadzu) and 10 mm cell.

THM was analyzed (Trihalomethane) by the following method. Depending on the sample, an appropriate amount was put in a glass bottle and agitated vigorously for approximately 20 sec. Next, pentane was added to the sample (ratio 1:1). Then after 30 minutes of settling, the sample was extracted. The extracted sample was analyzed using a GC/ECD (HP 5890 Series II, HEWLETT PACKARD)[14].

DOC filtered the sample through a pore size of 0.45 μm PVDF(Polyvinylidene Fluoride) and then measured the filtered sample with a TOC analyzer (TOC 5000, Shimadzu) which employs a combustion/non-dispersive detection method: The analyzer added 2-3 drops of 2N HCl to the sample. It ana-

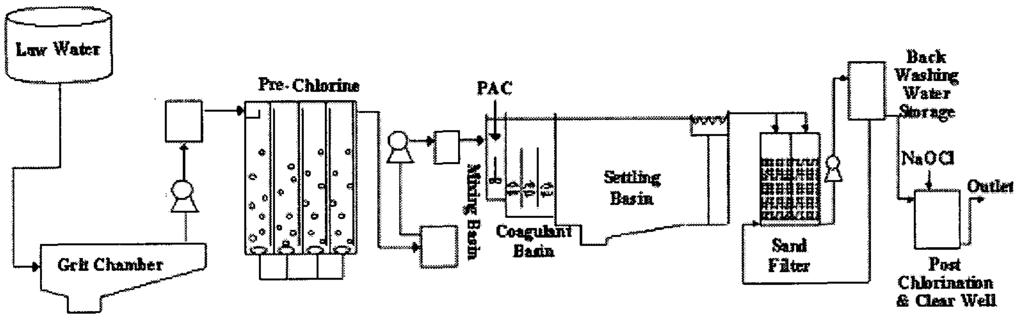


Fig. 1. Pilot Plant Schematic.

lyzed the sample in a NPOC (Non-purgeable Organic Carbon) mode, and was limited to a standard deviation (SD; standard deviation) of 200 and a coefficient variation (CV) of 2. The operation conditions for the TOC analyzer are shown in Table 1.

3. Result and discussion

3.1. Characteristics of DOC, UV_{220} and UV_{254} for raw water

DOC concentration of water is shown in Fig. 2 as 2.24 mg/L, TOC concentration exceeding 2 mg/L, and alkalinity is 41 mg of $CaCO_3$/L. The value of SUVA is less than 3. According to Edzwald [1993], when the value of SUVA is less than 3, compared to a higher SUVA (4-5), it is hydrophilic, non-aromatic, and low in molecular material.

The molecular weight distribution of organic matter, in the case of UV_{254} and K, and 9.3 %, 8.5 % for over 30 K. However, it was the highest when less than 1K which belonged to low molecule material at a ratio of 43-47 %, and it was the lowest for high molecular material at a ratio of 18.6-14.9 %. For UV_{220}, the index of biodegradable low molecular matter less than 0.5 K dominated at a ratio of 89.1 % and 4.2% for 0.5-1 K, 2.8 % for 3-10 UV_{220} was 16.7 %, 19.1 % for less than 0.5 K, 25.9 %, 27.9 % for 0.5-1 K, 22.2 %,˙23.4 % for 1-3 K, 16.7 %, 14.9 % for 3-10 K, 9.3 %, 6.4 % for 10-30 K, 3.8 % for over 10 K. Molecular distribution was 5-10 K and removed effectively by chemical coagulation and sedimentation. However, in the case of Han River water, most molecular weight was medium to low less than 10 K.

The results of the analysis to assess the correlation between UV_{254}, DOC, and THM are shown in Fig. 3, 4. The regression equations predicting the relationship between DOC and THM concentration are shown in equation 1, 2.

$$DOC = 44.78UV_{254} - 0.031 \quad (1)$$

$$THM = 0.008DOC + 0.00009 \quad (2)$$

Table 1. Operation conditions for the TOC-Analyzer

Items	Condition
TC catalyst	High sensitive
TC furnace temperature	680 ℃
Syringe size	250 μL
Number of washes	4
Number of injects	3
Max number of injects	4
Carrier gas	Pure-Air (N_2/O_2)
SD (standard deviation)	200
CV(coefficient of variation, %)	2

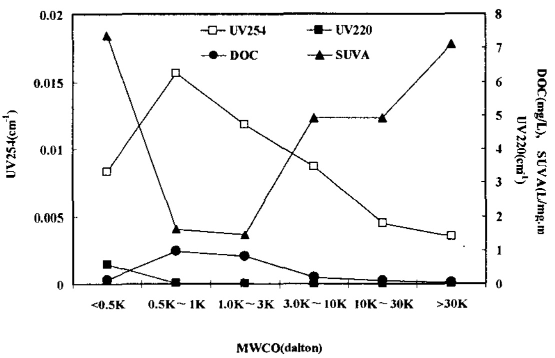


Fig. 2. Molecular weight distribution of UV_{254}, UV220, DOC and THMs for raw water.

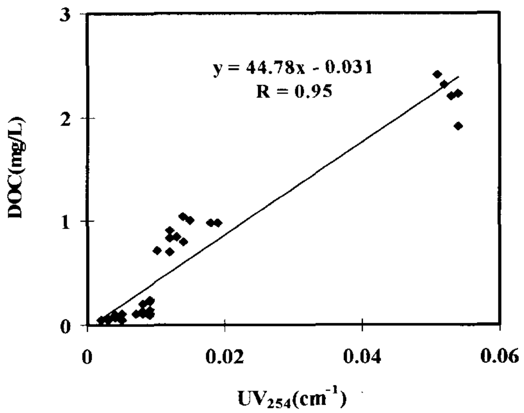


Fig. 3. Relationship between UV_{254} and DOC.

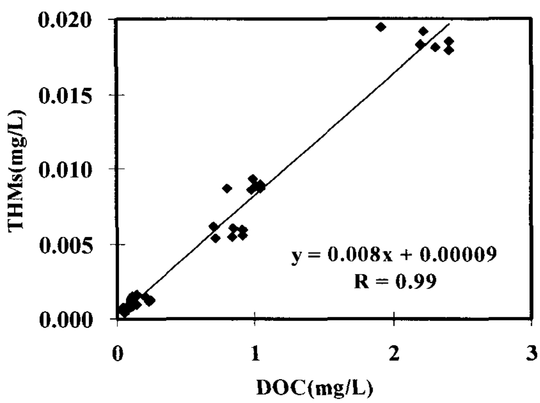


Fig. 4. Relationship between DOC and THMs.

3.2. Behavior of DOC and THMs based on Gt value

Deciding the value of G is very important in the operation of a coagulation process. It is thought that G values of 25-100 sec^{-1} for flocculation and Gt are favorable to the values 10^4-10^5 sec[15].

PAC was injected into a concentration of 16 mg/L which was the same concentration in this water facility, and contact time was 60 sec. This experiment was carried out by changing the G value to 500-1,100 sec^{-1}.

Fig. 5 shows the removal efficiency of DOC and turbidity for different Gt values after each process. The conditions for flocculation were to fix contact time to 30 min, resident time to 3.5 hrs during sedimentation, and water velocity to 40 cm/min. The highest removal ratio of DOC was 68.4 % when the Gt value was 42,000, and it was the lowest with a 40.9 % ratio when the Gt value was 30,000. The total removal ratio of DOC (77-84.2 %) was during coagulation/sedimentation. Most DOC was removed during the coagulation process. The filtration process had approximately 10 % removal efficiency for DOC regardless of the Gt value.

Turbidity removal was at its highest at 98.2 % at a Gt value of 66,000. In addition, according to the Gt values given in this experiment, removal efficiency was over 95 %. In contradiction to the DOC result, turbidity removed more than 20 % during filtration and therefore, it is thought that the turbidity removal ratio is excellent.

As shown in Fig. 6 and 7, the molecular weight

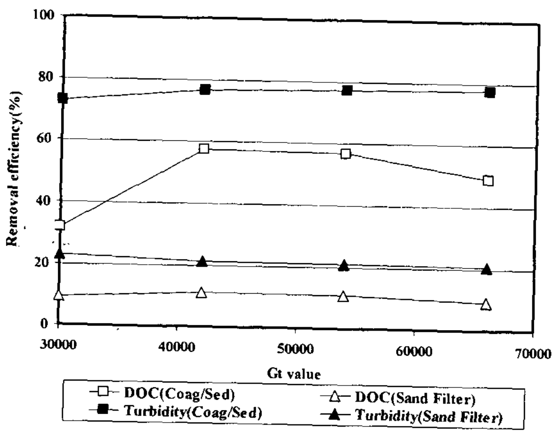


Fig. 5. Removal efficiency for DOC and turbidity according to Gt.

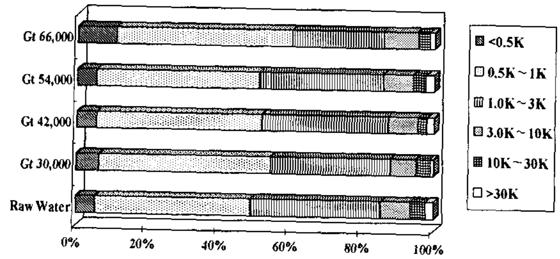


Fig. 6. DOC molecular weight distribution of coagulation/sedimentation according to Gt.

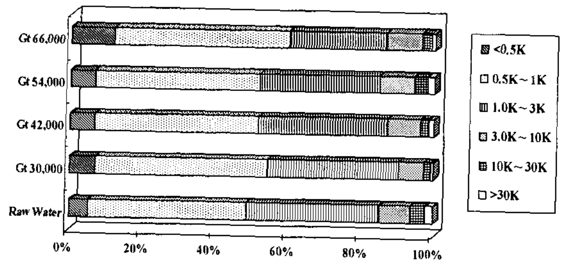


Fig. 7. DOC molecular weight distribution of filtration according to Gt.

distribution of raw water is as follows: 48.6 % less than 1 K, 45.1 % between 1 and 10 K, 4.0 % between 10 and 30 K, and 2.4 % over 30 K. This means that low and middle molecular weights were widely distributed, whereas high molecular weight was thinly distributed at 6.4 %. According to Jeong's research (1998), the molecular weight distribution of Han River water was 51.6 %, 1-10 K, >10K for <1K, 1-10 K, >10K, and the results of this research show similar results[16].

Molecular weight distribution under 1K occupied 54.3 % of the total, an increase of 11.7 % compared to 48.6 % for raw water, of which 1-10 K belonged to middle molecular weight and was 9.6 % effective in removal. In addition, high molecular distribution over 10 K was 18.5 % effective in removal.

Low molecular weight material less than 0.5 K increased by 3.1 % during coagulation/sedimentation at a Gt value of 66,000, and illustrated the lowest value of 1.2 % at a Gt value of 30,000. During coagulation/sedimentation, 50 % of most high molecular material over 10 K was removed and the highest at 57.4 % during coagulation/sedimentation at a Gt value of 42,000. During the filtration process, low molecular material under 0.5 K showed the highest value with an increase of 25.9 % at a Gt value of 54,000, and had the lowest value at 9.4 % at a Gt value of 30,000.

DBPs that occur due to chlorine disinfection are typically THM which are generated by chlorine reacting with humic matter in water. As we can see in Fig. 8, removal efficiency was highest when the Gt value was 42,000. At a Gt of 30,000 with the lowest removal ratio, the total removal ratio was 45.9 % (35.6 % for coagulation/sedimentation, and 10.3 % for filtration).

3.3. Behavior of DOC, UV_{220} and UV_{254} after Pre-chlorination

This research was performed to assess the behavior of DOC, UV_{220} and UV_{254} when pre-chlorination was applied to a conventional water system. Fig. 9 shows

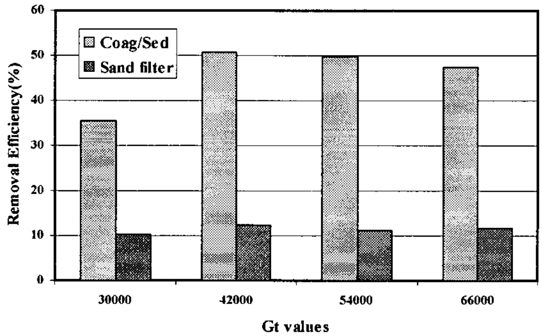
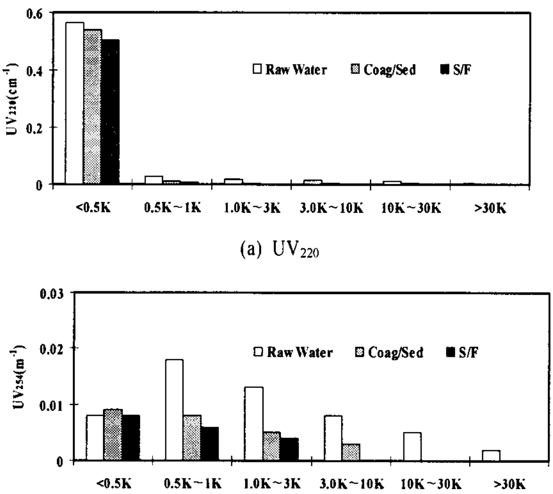


Fig. 8. THM removal efficiency according to Gt value.



(a) UV_{220}

(b) UV_{254}

Fig. 9. Molecular weight distribution of UV_{220} and UV_{254} after the pre-chlorination.

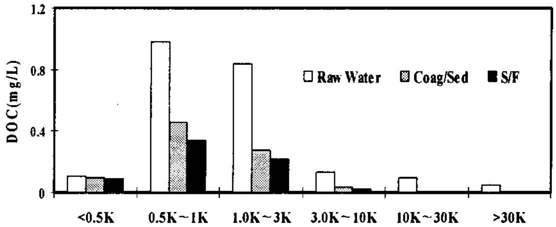


Fig. 10. Molecular weight distribution change of DOC after the pre-chlorination.

the variation of molecular weight distribution of UV_{220} and UV_{254} after pre-chlorination.

The removal efficiency of low molecular material (below 1 K) was 92.7 % for UV_{220} in raw water. This increased from 5.6 % to 98.3 % during coagulation/sedimentation and increased from 1.8 % to 99.6 % during filtration. Therefore, it is thought that matter with a low molecular weight less than 1K cannot be removed easily by a conventional water treatment system.

It was known through previous research that UV_{254} has an interrelationship with THM. The ratio of UV_{254} to THM for less than 1K was 49.0 % in raw water. Originally, it was 75.0 %. However, 26 % converted to low molecular weight material during coagulation/sedimentation. The ratio was 86.7 % during filtration. A high molecular weight for UV_{254} of over 10K was not detected by this test.

Fig. 10 shows the change in molecular weight distribution for DOC after pre-chlorination. DOC molecular weight distribution after pre-chlorination with a Gt value of 42,000 was examined and recorded as 49.2 %, low molecular weight matter under 1K was 63.2 % after coagulation/sedimentation, and 64.2 % after filtration. Molecular weight increased by 14 % after coagulation/sedimentation, but showed only a 1% increase post filtration. Matter having a high molecular weight of over 10K occupied 7.0 % of the raw water and 1.9 % during coagulation/sedimentation.

4. Summary

Matter less than 1K was mostly occupied in UV_{254} and DOC. DOC showed fair removal efficiency after pre-chlorination. THM removed 51 % and 12 % respectively for coagulation/ sedimentation and filtration using the selected conventional system.

When the Gt value was 42,000, the removal ratio of DOC was at its highest at 68 %. Most DOC (77-84 %) was removed during coagulation/sedimentation. A removal ratio of DOC at 15-23 % was illustrated during filtration. Turbidity removal ratio increased with the increase of the Gt value and therefore, turbidity removal efficiency reached 98 % at a Gt value of 66,000. When Gt values were between 30,000 and 66,000, levels used in this experiment, over 50 % of high molecular matter during coagulation/sedimentation were removed.

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