

Formation characterization and removal of disinfection by-products in water treatment processes

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Abstract This study evaluates the formation and removal of DBPs along with precursors in a pilot-scale treatment plant employing conventional treatment processes (coagulation/ sedimentation/filtration), ozonation and granular activated carbon (GAC) treatment with three EBCT (10 min, 15 min, 20 min) and three types of GACs (coal-based F400, coal-based SLC, coconut-based SLC-2000). Pilot-scale study suggested that the GAC adsorber demanded more than EBCT 15 min for DBPs removal and exhibited excellent performance for HAA removal. During approximate a one-year pilot scale evaluation for ozone/GAC processes, as high efficiency of removal was continued, exchange cycle and regeneration life of GAC need to be decided through longer operation.

Keywords Activated carbon adsorption; disinfection by-products (DBPs); haloacetic acids (HAAs); ozonation; trihalomethanes (THMs)

Introduction

Aquatic humic substances in water generate potentially harmful disinfection by-products (DBPs) such as haloacetic acids (HAAs) and trihalomethanes (THMs) during chlorination. As part of the 1986 amendments to the Safe Drinking Water Act, the US Environmental Protection Agency (US-EPA) has proposed the Disinfectants/Disinfection By-products (D/DBP) Rule, which contains two stages (I and II). Under Stage I of the D/DBP Rule, US-EPA would set maximum contaminant levels (MCLs) for total trihalomethanes (THMs) at 80 µg/L, for a total of five haloacetic acids (HAA5) at 60 µg/L, for bromate at 0.010 mg/L, and for chlorite at 1.0 mg/L. Proposed Stage II MCLs for THMs and HAA5 are 40 and 30 µg/L, respectively. Existing Korean regulations would set THMs at 100 µg/L.

The best available technology (BAT) to meet Stage I THMs and HAA5 MCLs includes enhanced coagulation or granular activated carbon (GAC) adsorption with an empty-bed contact time (EBCT) of 10 minutes. BAT for meeting the Stage II DBP requirements includes GAC adsorption and membrane filtration. Drinking water utilities are preparing for major changes due to the proposed regulations for DBPs.

The Buyeo Water Treatment Plant (BWTP) was located at the middle and lower part of the Keum River in Korea and exhibited many problems for conventional water treatment processes for removing high concentrations of organic matter and ammonia from source water. Especially, some modifications for the existing treatment processes are needed to achieve the reduction of DBPs including THMs and HAAs generated during chlorination. Thus, this study evaluated the formation and removal of DBPs along with precursors in a pilot-scale treatment plant employing conventional treatment processes (coagulation/ sedimentation/ filtration), ozonation and granular activated carbon (GAC) treatment.

Materials and methods

Source water

The source water for the BWTP comes from the Keum River water. The water is of varying quality, with seasonal turbidity and temperature swings. The quality of the raw water from 1 February 1998 to 31 December 1999 is summarized in Table 1, which shows average values for source water. As is apparent, the range of $\text{NH}_3\text{-N}$ in water from Keum River was 0.0–3.2 mg/L, and the $\text{NH}_3\text{-N}$ concentration was detected as high as 3.2 mg/L in the winter.

The pilot plant

The pilot plant was equipped with six granular activated carbon (GAC) adsorption columns as well as ozone oxidation process and conventional water treatment processes such as coagulation, flocculation, sedimentation and filtration. This was the scaled-down prototype of the present full-scale water treatment plant. An explanatory sketch of the pilot plant is shown in Figure 1.

The capacity of pilot plant which consisted of two parallel systems was 240 m³/day. The operation duration of the system A was about one year from 1 February–31 December 1999. The operation duration of system B was about two years from 1 February 1998 to 31 December 1999.

Chlorine was added prior to rapid mixing tank in system A to break-point pre-chlorination that used for ammonia removal. The ozone/air mixture from the ozone generator in the main plant was applied through a nozzle into the ozone treatment column. This is equivalent to an ozone dosage of about 1–3 mgO₃/L for the remaining residual ozone dosage 0.2 mgO₃/L.

The study made use of the six GAC filters, each of which was designed, for 40m³/day.

Table 1 Water quality characters of source water

| | Temp. (°C) | pH | Turbidity (NTU) | KMnO ₄ Demand (mg/L) | NH ₃ -N (mg/L) | SS (mg/L) |
|-----------|------------|-----|-----------------|---------------------------------|---------------------------|-----------|
| Maximum | 32 | 9.3 | 500 | 23 | 3.2 | 1,141 |
| Minimum | 3 | 6.8 | 3.5 | 3.3 | 0.0 | 2 |
| Mean | 17 | 7.4 | 22 | 10.2 | 0.6 | 30 |
| 95% value | 30 | 8.6 | 60 | 16.2 | 1.7 | 120 |

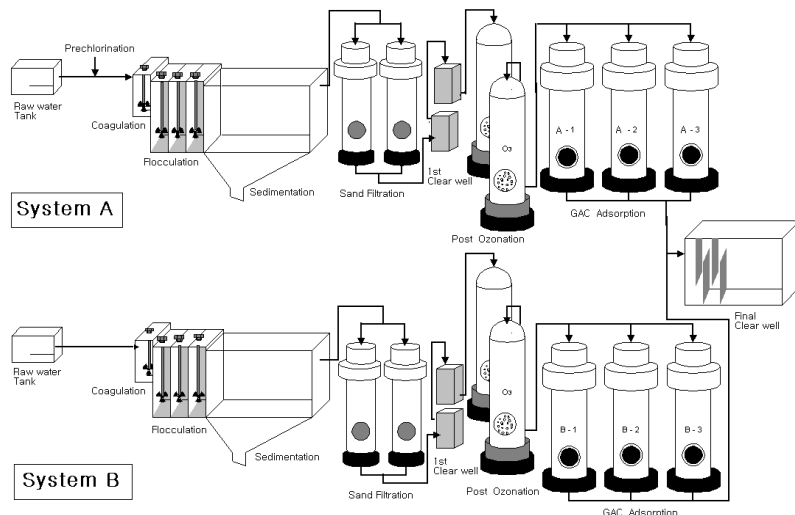


Figure 1 Schematic diagram of Buyeo water treatment pilot plant

Each of the system A contained a different EBCT, referred to as 10 min, 15 min, 20 min and each were operated with coal-based SLC. Each of the system B contained a different GAC, referred to as coal-based F-400, coal-based SLC, coconut-based SLC-2000 and each was operated under an EBCT of 15 minutes. Three different types of GAC were evaluated for the verification of the pilot scale protocols. The characteristics of GAC is shown in Table 2.

Methods

In this study analytical method of total organic carbon (TOC) and dissolved organic carbon (DOC), total organic halide (TOX), THMs, HAA5 was listed in Table 3. NOM fractionation was carried out using a modified resin isolation and fraction procedure originated by Leenheer (1981). Pre-filtered water samples were processed through XAD-8 followed by XAD-4 resins to isolate hydrophobic (XAD-8 adsorbable), transphilic (XAD-4 adsorbable), and hydrophilic (neither XAD-8 nor XAD-4 adsorbable) NOM fractions. The procedure for adsorbable DOC (ADOC) and biodegradable DOC (BDOC) determination followed the technique used by Kim *et al.* (1997).

Results and discussion

The NOM structure and DOC fraction information for raw and treated waters by each process are summarized in Table 4. This showed that conventional treatment processes preferentially removed hydrophobic NOM fraction and the hydrophilic NOM fraction was preferentially removed by a GAC filter. On a DOC fraction, hydrophobic and adsorbable

Table 2 Characteristics of GAC

| Parameters | SAMCHULLEE | CALGON | F-400 |
|----------------------------------|----------------|----------------|----------------|
| | SLC | SLC-200 | |
| Raw material | Coal | Coconut | Coal |
| Effective size (mm) | 0.8~0.9 | – | 0.55~0.75 |
| Mesh size | 8 × 30 | 8 × 30 | 8 × 30 |
| | ≥ 2.38 mm ≤ 3% | ≥ 2.38 mm ≤ 1% | ≥ 1.68 mm ≤ 5% |
| | ≤ 4.59 mm ≤ 2% | ≤ 4.59 mm ≤ 1% | ≤ 0.42 mm ≤ 4% |
| Mean particle dia. (mm) | 1.57~1.7 | – | 0.9~1.1 |
| Dry weight (%) | 1.7 | 2.0 | ≤ 2 |
| Hardness (%) | ≥ 97 | 98.9 | ≥ 90 |
| Uniformity coefficient | – | – | 1.5~1.9 |
| ρ_b (g/cm ³) | – | 0.48 | 0.45 |
| Surface area (m ² /g) | ≥ 1,100 | – | 1,050~1,250 |
| Iodine number (mg/g) | 1,137 | 1,185 | ≥ 1,050 |
| Pore volume (cc/g) | – | – | 0.85~0.95 |

Table 3 Analytical method

| | Analyzed parameter | Formula | Analytical methods |
|-----|-----------------------|-------------------------------|--------------------|
| TOX | Total organic halides | – | SM* 5320B |
| | Chloroform | CHCl ₃ | |
| THM | Bromodichloromethane | CHCl ₂ Br | EPA 502.2 |
| | Dibromochloromethane | CHClBr ₂ | |
| | Bromoform | CHBr ₃ | |
| | Monochloroacetic acid | CH ₂ ClCOOH (MCAA) | |
| HAA | Dichloroacetic acid | CHCl ₂ COOH (DCAA) | Modified EPA 552 |
| | Trichloroacetic acid | CCl ₃ COOH (TCAA) | |
| | Monobromoacetic acid | CH ₂ BrCOOH (MBAA) | |
| | Dibromoacetic acid | CHBr ₂ COOH (DBAA) | |
| TOC | Total organic carbon | – | SM* 5310C |

* SM = Standard Methods

Table 4 NOM structure and DOC fraction information for raw and treated waters

| Waters (%) | Hydrophobic NOM | Transphilic NOM | Hydrophilic NOM | ADOC ^a | A&BDOC ^b | BDOC ^c | NRDOC ^d |
|-------------|--------------------|--------------------|--------------------|-------------------|---------------------|-------------------|--------------------|
| Raw | 50.6 | 22.4 | 27.1 | 72.1 | 10.4 | 9.1 | 8.4 |
| Filtered | 41.9 | 23.8 | 34.3 | – | – | – | – |
| Ozonated | 32.3 | 33.1 | 34.7 | 67.7 | 16.9 | 11.8 | 3.7 |
| GAC treated | 41.5 | 36.7 | 21.9 | 72.4 | 10.5 | 9.2 | 8.4 |

^a Adsorbable DOC; ^b Adsorbable & biodegradable DOC; ^c Biodegradable DOC; ^d Nonremoval DOC

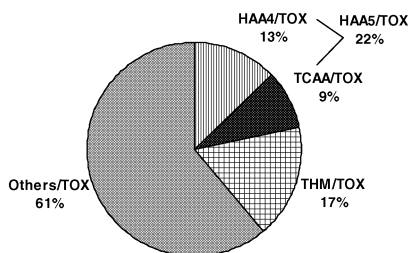
fractions decreased only slightly with ozone treatment. The change of DOC fraction indicated that some biological oxidation of the precursors was occurred by ozonation.

THMs and HAAs were the major contributors to TOX, accounting for approximately 39% of the observed TOX in filtered water. A comparison is provided in Figure 2. THMs and HAAs were showed to be the major contributors to TOX with respective contributions of 17% and 22%.

Tables 5 and 6 show the average TOC and DBPFPs concentrations for source and treated water during operation. For data shown in Table 5, the THMFP and HAAFP was 128.3 µg/L and 170.9 µg/L, respectively. Results presented for DBPs formation potential suggest that application of GAC is needed for controlling DBPs because conventional treatment processes such as a coagulation/sedimentation/filtration is unable to achieve the required degree of removal of DBPs and DBP precursors.

The breakthrough curves of THMFP and HAAFP for different GACs and EBCTs are showed in Figures 3 and 4. Results presented indicate that ozonation is unable effectively to remove organics and DBPs precursors at ozone dosage of 1~3 mg O₃/L (0.5~1.0 mg O₃/mg DOC).

As seen in Figure 4, no HAAFP breakthrough was observed on system A and system B until after 11 months of operation. Removal capacity of HAAFP was more effective than that of THMFP for different GACs and EBCTs. The highest capacity for THMFP removal was obtained by coal-based GAC.

**Figure 2** Various DBPs fractions for filtered water**Table 5** Mean TOC and DBPFPs for source and treated waters during operation (February–December 1999) at system A

| Waters (µg/L) | TOC (mg/L) | THMFP | TCAA FP | HAA5 FP |
|---------------|------------|-------|---------|---------|
| Source | 4.2 | 128.3 | 93.0 | 170.9 |
| Filtered | 3.2 | 82.2 | 77.4 | 133.6 |
| Ozonated | 2.8 | 87.3 | 60.0 | 103.0 |
| GAC treated | | | | |
| EBCT 10 min. | 1.9 | 59.0 | 30.1 | 54.7 |
| EBCT 15 min. | 1.6 | 34.4 | 19.4 | 38.3 |
| EBCT 20 min. | 1.4 | 18.8 | 16.6 | 32.5 |

Table 6 Mean TOC and DBPFPs for source and treated waters during operation (February 1998–December 1999) at system B

| Waters ($\mu\text{g/L}$) | TOC* (mg/L) | THMFP | TCAAFFP* | HAA5FFP* |
|----------------------------|-------------|-------|----------|----------|
| Source | 4.2 | 128.3 | 93.0 | 170.9 |
| Filtered | 3.0 | 76.5 | 77.4 | 133.6 |
| Ozonated | 2.5 | 52.6 | 60.0 | 103.0 |
| GAC treated | | | | |
| Coal (F-400) | 1.6 | 29.5 | 21.4 | 45.3 |
| Coal (SLC) | 2.0 | 25.4 | 18.2 | 43.9 |
| Coconut (SLC-200) | 2.1 | 46.5 | 20.3 | 43.1 |

* Data: February–December 1999

The data show that the temperature of surface water in the Keum River fluctuates widely during the year, ranging from 3° during the winter months to 32° during the summer months. These results showed that, during the low temperature period, the temperature had no direct impact on the removal of THMFP and HAAFP.

Figure 5 shows the TOX, THMs and HAAs breakthrough curve for coal based SLC at different EBCTs. It is evident that the increase in EBCT produces a more effective reduction of TOX and THM. THMs breakthrough occurred after five months of operation for EBCT 10 min, after seven months of operation for EBCT 15 min, and after nine months of operation for EBCT 20 min. As seen in Figure 5, no HAAs breakthrough was observed on system A until after ten months of operation, and HAA removal capacities for different EBCTs was shown similarly. The Ozone process had not only very poor DBP precursor removal capacity but also DBP removal capacity.

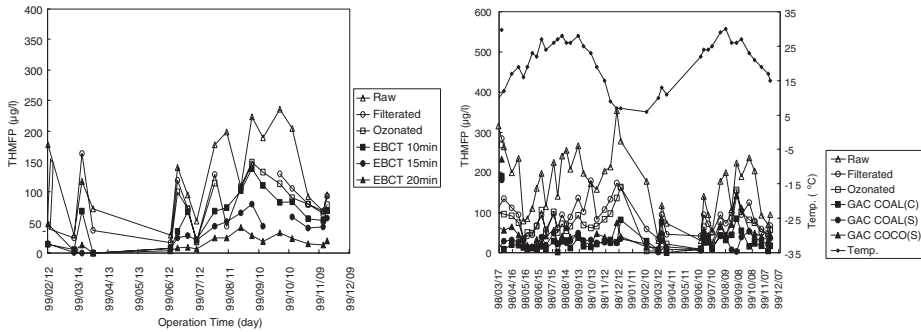


Figure 3 THMFP data profiles for raw and treated waters at system A (GAC as a function of EBCT) and system B (GAC as a function of carbon type)

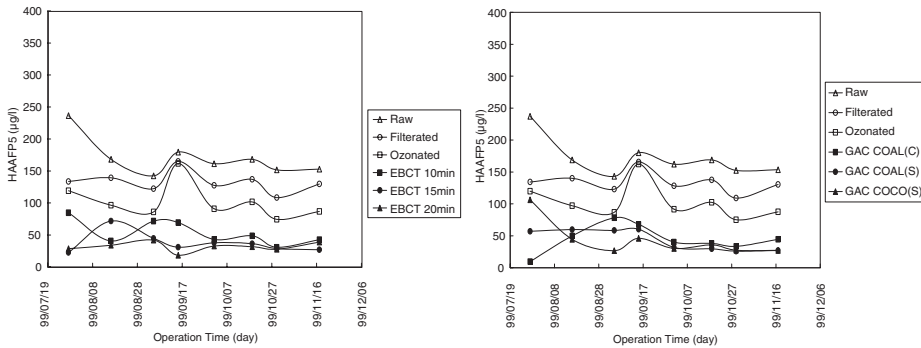


Figure 4 HAAFP data profiles for raw and treated waters at system A (GAC as a function of EBCT) and system B (GAC as a function of carbon type)

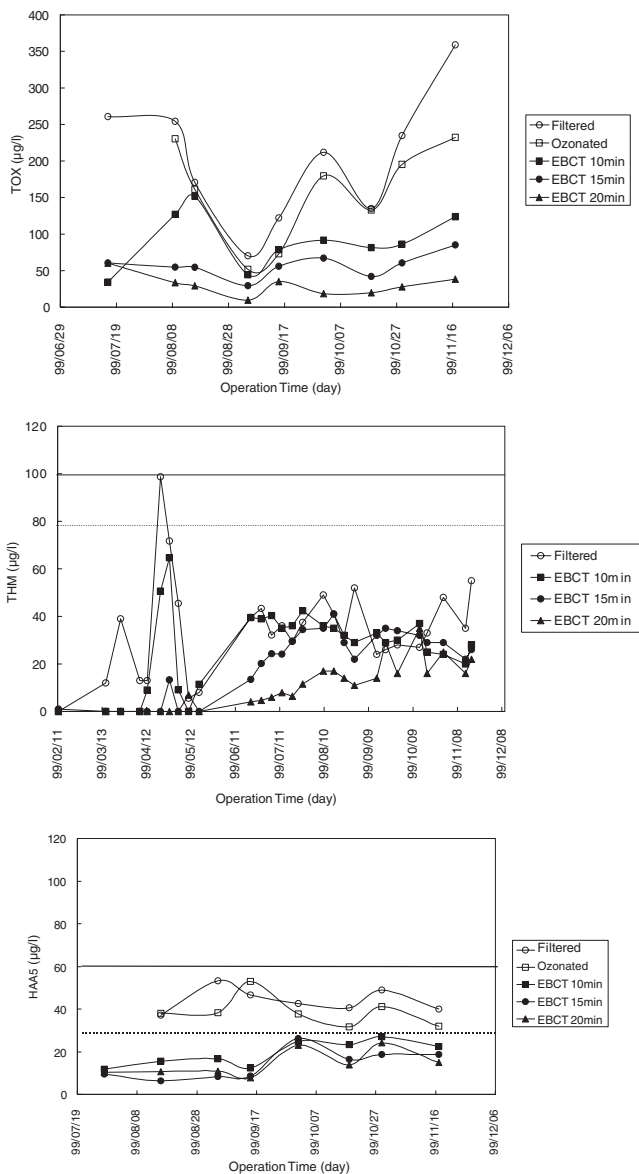


Figure 5 TOX, THM, HAA data profiles for treated waters at system A (GAC as a function of EBCT)

Figure 6 summarized average concentration of the TOX, THMs and HAAs for different processes and GAC filter at system A during the BWTP operation period. EBCT 20 min achieved, on average, removal of 81%, 70% and 63% of TOX, THMs and HAAs, respectively, whereas ozonation had very poor THM and HAA removal.

Conclusion

THMs and HAA5 did not reach the levels of risk. However, it is difficult to achieve compliance with the new regulations based on THMFP and HAAFP [THMs 80 µg/L, HAAs 60 µg/L by the Stage I D/DBP Rule (2001)]. Thus, BWTP needs to introduce GAC treatment in conventional water treatment plant. Pilot-scale study suggested that GAC adsorber demanded more than EBCT 15 min for DBPs removal and exhibited excellent performance for HAA removal. During approximate one year pilot scale evaluation for ozone/GAC

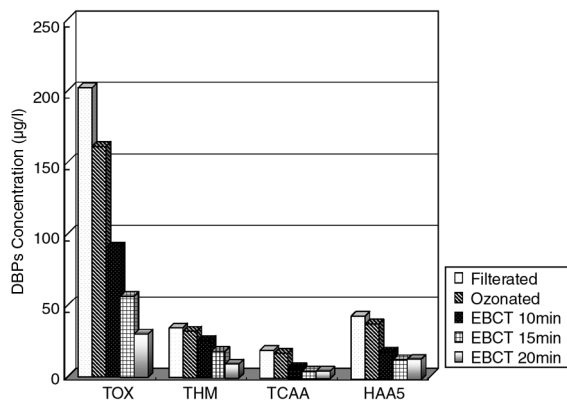


Figure 6 Mean concentration of DBPs for filtered, ozonated and GAC treated waters during operation (February–December 1999) at system A

processes, as high efficiency of removal was continued, exchange cycle and regeneration life of GAC need to be decided through longer operation.

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