Ozonation of Han River humic substances

M.J. Yu, Y.H. Kim*, I. Han and H.C. Kim

Department of Environmental Engineering, University of Seoul, 90 Junnondong, Dongdamungu, Seoul, 130–743, Korea

*Department of Environmental Management, Shinheung College, Howondong, Euijungbusi, Kyungido, 480–701, Korea

Abstract This study investigated the characteristics of extracted humic substances (HS) which are ubiquitous in river waters and affect the treatment of the water. HS were extracted from the Han River and the samples obtained were analyzed before/after oxidation with the following analytical methods: DOC, THMFP, UV-abs, chemical composition, molecular weight distribution, IR. Ozonation experiments were conducted in batch-type reactors. Ozone dose was 1 mg/L and contact time was varied from 0 to 20 minutes. The fraction of hydrophobic matter was 56.0% of total organic carbon in the Han River and the ratio of humic/fulvic acids was 22.4/77.6, showing high fractions of aromatic and/or double carbon bond functional groups and high fractions of saturated aliphatic carbons. Oxygen fraction of Han HS was relatively high compared with other humic substances (Suwannee River humic and fulvic acids), which are consistent with the results of IR spectra. The IR spectra showed the increase in aliphatic groups by ozonation of the Han HS. Humic substances could not completely be oxidized to CO_2, H_2O etc., but were partly oxidized to low molecular weight matter (aliphatics, aldehydes, carboxylics, polysaccharides etc.), so low removal efficiencies in terms of DOC (31~35% with 5 minute contact) were observed. For UV_{254}, 5 minute or shorter contact showed more than 80% removal efficiencies.

Keywords AMW; fulvic acid; Han River humic substances; humic acid; IR, ozonation

Introduction

Humic substances (HS) existing in waters may originate from the soil or be formed in the water, resulting from polymerization and degradation, biological and/or photochemical, of vegetable substances. Humic substances consist of humic and fulvic acids (HA and FA) and human (Aiken *et al.*, 1985; Thurman, 1985) In general, natural water with HS is yellowish brown. According to Flaig (1963), chemicals involved in the formation of HS are carbohydrates (50~60%), lignins (10~30%), proteins (1~3%) and some phenolic compounds. Many researchers have investigated structural features of HS with various methods such as NMR, IR and GC/MS (Pihlaja, 1991; Norwood *et al.*, 1980; Reckhow *et al.*, 1990). Some dissolved organic matter is not easily removed with the conventional water treatment processes (Rook, 1976; 1977). Humic substances are precursors of disinfection by-products (DBPs) including THMS. Among THMs, $CHCl_3$ is considered as the most toxic and carcinogenic compound (Tardiff, 1975; Weisburg, 1977). The amount of THMs produced is proportional to the precursor concentration. Therefore, many techniques were proposed to reduce the formation of THMs in the processes of the conventional water treatment (Symons, 1981). To reduce the formation of THMs in drinking water treatment processes, it is effective to apply ozonation and GAC adsorption to the water treatment. In addition to reduction of THMs, ozonation and GAC adsorption processes have advantages in removing other micropollutants. There are two reaction pathways, between dissolved HS and ozone in the water. Ozone molecules react directly with nucleophilic or radical initiation sites, or OH radicals react with propagator or initiator sites. Only small portions of HS dissolved in natural waters can be completely oxidized by ozonation. Some portion of degraded matter increases polarity and hydrophilicity in the solution and its structure can

21

be transformed to easily biodegradable matter (Masschelein, 1982; De Laat *et al.*, 1991). Te purpose of this research is to investigate the characteristics of HA and FA extracted from the Han River in comparison with the Suwannee River HA and FA from IHSS. The relationship between apparent molecular weight and various parameters such as DOC, UV-abs and THMFP was investigated using a batch-type ozonation reactor.

M.J. Yu *et al.*

Materials and methods

Extraction and isolation of HS. Extracted and isolated HS from the Han River was using the methods reported by Thurman and Malcolm (1981). The resin used was Amberite-XAD7HP from Rohm & Haas company. The resin was filled in a glass column (ID:3 cm) up to 40 cm. 50 L of the water was passed through the glass column with flow rate of 8~10 mL/min. To extract HS sorbed in the resin bed 0.1 N NaOH was used. HA and FA were then isolated from the solution. Na^+ ions in the solvent were substituted with H^+ using Amberite IRC-50, followed by freeze-drying to obtain HS. The freeze-dried HS was used for preparation of the HS stock solution.

Ozonation of HS solutions. The ozonation apparatus consists of a glass ozone contractor (ID 6 cm × H 45 cm), an ozone generator and an oxygen tank. Samples with low (5 mg/L) and high (100 mg/L) concentrations of HS were prepared for ozonation. Ozone was dosed into the ozone reactor to be dissolved 1 mg/L per minute for 1~20 min. The minimum contact time required to obtain relatively constant concentration of HS was 5 min for the low concentration samples and 10 min for the high concentration samples.

Distribution changes of apparent molecular weight (AMW) by ozonation. To determine the distribution changes of AMW of HS (5 mg/L) with samples obtained before/after ozonation were filtered with membrane and molecular sieves such as 0.45 µm and 100 K, 10 K and 1 K dalton.

IR spectrum change of HS by ozonation. IR spectra were obtained by scanning HS powders obtained before/after ozonation of the high HS concentration solutions. KBr (FT-IR Grade, Aldrich Co.) was mixed with HS in the ratio of 100 to 1 and the IR spectra of the mixture was scanned by IR spectrophotometer (Bruker IFS 120HR FT-IR).

Determination of physicochemical characteristics of HS. DOC of the solutions obtained before/after ozonation was determined with TOC analyzer (DC-180, Dohrmann, USA) after filtration of the samples with 0.45 µm membrane filters. A UV-spectrophotometer (Hitachi 150–20, Japan) was used to determine the absorbance at 254 nm. For THMFP experiment, solutions were chlorinated at pH 8 and at 20°C for 48 hr. Using the head space method, volatile compounds in samples were concentrated and injected to a GC (HP-5890, Hewlett Packard, USA). Elemental composition of HS was analyzed with an element analyzer (EA1108 CHNS/O Mode, Fisons Instrument, Italy).

Results and discussion

Extraction and isolation of HS

Han River water (DOC concentration was initially 4.6 mg/L) was filtered through Amberite-XAD7HP resin column until no change of DOC concentration (2.0 mg-DOC/L) was observed. Extracted amount of HS was 2.5 mg/L in the water. Table 1 compares the values in the literature with the results of this experiment. Extracted HS from the Han River consists of humic (22.4%) and fulvic (77.6%) acids. This composition ratio is comparable with the other values of different sources (Keum River water and Soyang Lake water). The

22

Table 1 Comparison of HS compositions from different sources

| Items	Conc. (mg/L)				
	Han River water	*Keum River water	*Nakdong River water	*Daechung Lake water	*Soyang Lake water
HS	2.5	0.6	2.5	0.4	0.2~0.8
(HS/DOC, %)	(56.0)	(48.1)	(78.0)	(60.5)	(20~30)
HA	0.6	0.2	1.8	0.1	0.05~0.2
(HA/HS, %)	(22.4)	(28.2)	(28.0)	(32.9)	(15~25)
FA	1.9	0.4	0.7	0.3	0.2~0.6
(FA/HS, %)	(77.6)	(71.8)	(72.0)	(67.1)	(75~85)

*MOE, 1995

hydrophobic fraction in TOC of Han River HS was 56.0%, much larger than that of Soyang Lake water (20~30%), an upper stream of the Han River. As shown in Table 1, Nakdong River water shows the highest hydrophobic fraction (78%). This high hydrophobic fraction indicates that Nakdong River water has many pollution sources. Comparing with IHSS (International Humic Substances Society) HA/FA, Han River HS shows a smaller carbon fraction and much higher oxygen fraction. The high oxygen fraction implies higher concentrations of -COO$^-$ and -OH functional groups in Han River HS. The results are summarized in Table 2.

Ozonation of HS

Distribution changes of AMW by ozonation. The AMW changes of HS were analyzed depending on THMFP, DOC and UV$_{254}$. The results are shown in Figures 1–3. In Figures 1–3, the portions of THMFP, UV$_{254}$ and DOC in the ranges of AMW after ozonation were calculated in the comparison with the corresponding values in the AMW range before ozonation. The portion of THMFP-causing materials below AMW 1,000 dalton shows approximately 40%, in the range of 10,000–100,000, 14% and in the range of 1,000~10,000

Table 2 Elemental composition of HS (dr wt.)

Elements HS	C (%)	H (%)	N (%)	O (%)
IHSS HA (The Suwannee River)	49.15	2.82	2.18	45.85
IHSS FA (The Suwannee River)	49.73	3.97	1.33	44.97
Han River HS	27.73	3.00	0.94	68.33
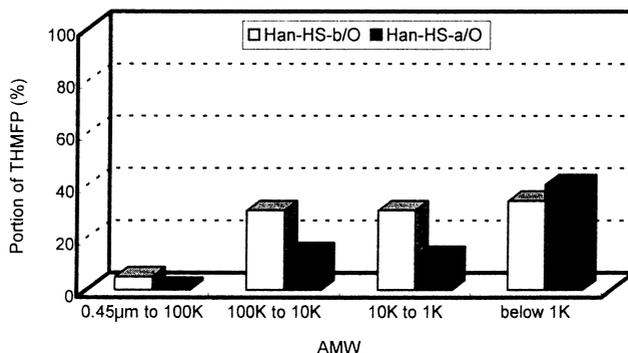
Figure 1 AMW distribution changes of THMFP-causing materials in Han HS solution by ozonation (b/O and a/O mean before and after ozonation, respectively)
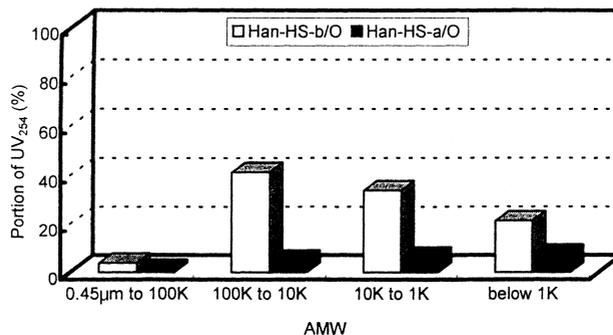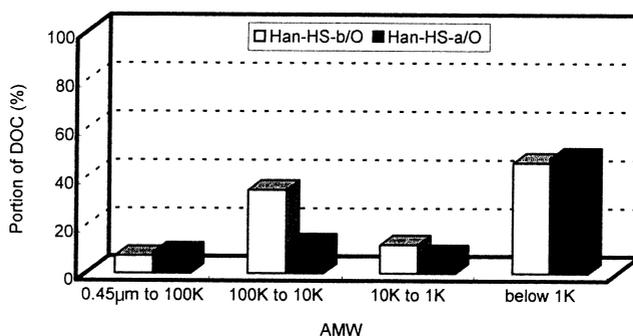
Figure 2 AMW distribution changes of UV_{254}-causing materials in Han HS solution by ozonation (b/O and a/O mean before and after ozonation, respectively)

Figure 3 AMW distribution changes of DOC-causing materials in Han HS solution by ozonation (b/O and a/O mean before and after ozonation, respectively)

shows 13% after ozonation. More than 90% of the THMFP-causing materials was below 100 K dalton. In the case of UV_{254}-causing materials, removal efficiencies were high over all the fractions of AMW. The AMW portion of DOC-causing materials below 1,000 dalton increased after ozonation, indicating incomplete oxidation. That is, mineralization and increase in the fraction of low molecular weight was observed.

DOC, UV_{254} and SUVA changes by ozonation. The removal efficiencies of HS depending on contact time (0–20 min) are shown in Figure 4. The removal efficiencies of DOC were 31–35% by 5–20 min ozone contact and those of UV_{254} were 83% by 5 min contact. Because DOC is not completely oxidized but transformed to intermediates of low molecular weight, showing resistance to ozonation, the removal efficiencies of DOC were always
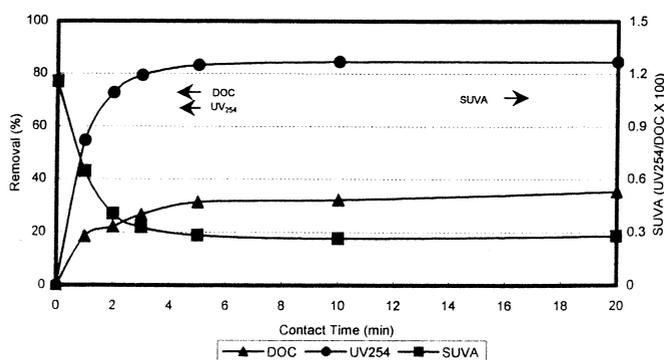

**Figure 4** Removal of Han River HS by ozonation

low. The SUVA (specific UV absorbance) as a parameter of humification is defined by UV_{254}/DOC ($100 \times m^{-1}$/mg/L). The SUVA of Han River HS was relatively low, compared with Daechung Lake water (1.72) and Keum River water (1.76), indicating that Han River HS has less aromatic functional groups and less double-bonded carbon groups. Therefore, it might mean that Han River HS is more easily biodegradable.

The decrease in THMFP was, in spite of low removal efficiencies of DOC by ozonation, possibly explained the transformation of large molecules to small ones.

IR spectrum changes by ozonation. The IR spectra mainly show the existence of oxygen-containing functional groups. The IR spectra of HS before and after ozonation are shown in Figure 5. The spectrum of 3420 cm^{-1} shows O-H vibration of carboxylic and alcoholic groups. This peak was moved to 3435 cm^{-1} and somewhat increased after ozonation. The double peak of 2966 cm^{-1} shows asymmetric and symmetric C-H stretching of the aliphatic groups. The peak was moved to 2959 cm^{-1}, 2926 cm^{-1} and the absorbances somewhat
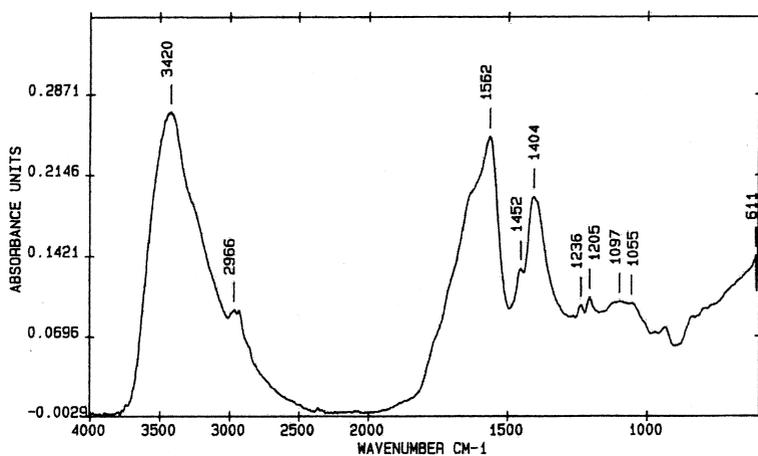
(a) before ozonation
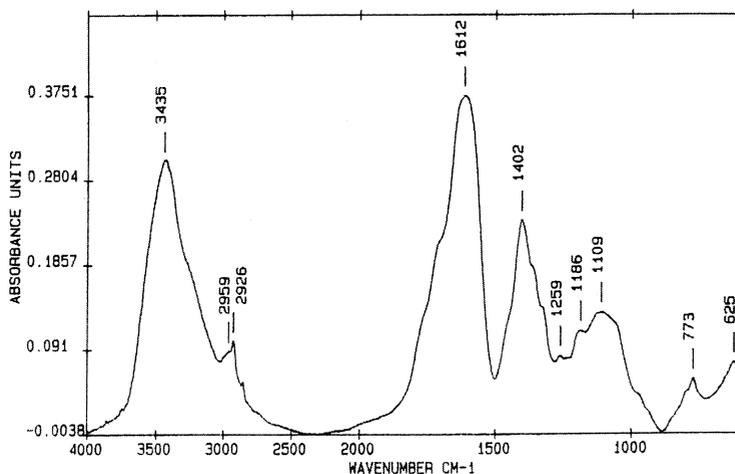
(b) after ozonation

Figure 5 IR spectra of the Han HS solution before/after ozonation

25

increased after ozonation. The spectrum at 1562 cm^{-1} shows aromatic C=C stretching vibration and H-bonded C=O stretching. This peak was moved to 1612 cm^{-1} after ozonation. The peak of 1452 cm^{-1} showing -CH$_2$ and -CH$_3$ vibration disappeared after ozonation. The region of 1055–1236 cm^{-1} which appears due to the polysaccharides, silicate vibration and C-O stretching, was reduced after ozonation. In summary, ozonation changed the structural characteristics of Han River HS in addition to removal of THMFP, DOC- and UV$_{254}$-causing materials depending on the AMW ranges.

Conclusions

1. Because the structure of extracted HS from the Han River has less aromatic compounds and double-bonded carbon groups, Han River HS is considered as an easily biodegradable compound.
2. The elemental composition of extracted HS from the Han River compared with other humic solutions (humic and fulvic acids from IHSS) shows lower carbon fraction and much higher oxygen fraction. This result was consistent with the result from IR spectra (much higher in functional groups containing -COO$^-$ and -OH).
3. Because DOC-causing materials were not oxidized completely by ozonation but accumulated by smaller AMW materials (aliphatic compounds, aldehydes, carboxylic acids, polysaccharides), the removal efficiency of DOC-causing materials was low.
4. HS extracted from the Han River, in terms of DOC and THMFP, showed a trend of mineralization and low molecularization in high AMW range and aliphatic, alcoholic and carboxylic groups were increased.

References

Aiken, G.R., Mcknight, D.M. and Wershaw, R.L. (1985). *Humic substances in soil, sediment and water, geochemistry, isolation and characterization*. Wiley Inc., 1–12.

De Laat, J., Dore, M. and Mallevialle, J. (1991). Effects of preozonation on the adsorbability and the biodegradability of aquatic humic substances and on the performance of granular activated carbon filters. *Wat. Res.,* **25**, 151–164.

Flaig, W. (1963). The chemistry of human substances. *Report of the FAO/AIWA Technical Meeting*, 103–127.

Masschelein, W.J. (1982). *Ozonation manual for water and wastewater treatment*. Wiley-Interscience, 63–65.

Ministry of Environment, Ministry of Construction and Transportation (1995). Development of advanced water treatment system. Korea.

Norwood, D.L., Johnson, D.J., Christmas, R.F., Hass, J.R. and Bobenrieth, M.J. (1980). Reactions with selected aromatic models of aquatic humic material. *Environ. Sci. Technol.*, **14**, 187–190.

Pihlaja, K. (1991). Humic substances in the aquatic and terrestrial environment, in *Lecture Notes in Earth Sciences*, Springer, Berlin, 113–121.

Reckhow, D.A., Singer, P.C., Malcolm, R.L. (1990). Chlorination of humic materials: Byproduct formation and chemical interpretations. *Environ. Sci. Technol.* **24**, 1655–1664.

Rook, J.J. (1976). Haloforms in drinking water, *AWWA*, **68**, 168–172.

Rook, J.J. (1977). Chlorination reactions of fulvic acids in natural waters. *Environ. Sci. Technol.* **11**, 168–172.

Symons, J.M. (1981). Treatment techniques for controlling trihalomethanes in drinking water. EPA-600/2 81/156.

Tardiff, R.G. (1975). Preliminary assessment of suspected carcinogens in drinking water. Interim Report to Congress. Appendix VII, U.S. EP, Washington D.C.

Thurman, E.M. (1985). *Organic geochemistry of natural water*. Martinus Niijhoff/Dr. W. Junk Publishers, Dortmund.

Thurman, E.M. and Malcolm, R.L. (1981). Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.*, **15**, 463–466.

Weisburg, E.K. (1977). Carcinogenicity study on halogenated hydrocarbon, *Environ. Health Perspec.* **21**, No. 7.