

Characterization of aquatic humic substances to DBPs formation in advanced treatment processes for conventionally treated water

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Abstract

An advanced water treatment demonstration plant consisted of ozone/granular activated carbon processes was operated to study feasibility of the processes. Natural organic matter (NOM) from raw and process waters at the demonstration plant was isolated into humic and non-humic fractions by physicochemical fractionation method to investigate characteristics of humic fraction (i.e., humic substances, HS) as a predominant haloform reactant. Ozone did not significantly oxidize the carboxylic fraction (from 39.1 to 35.9%), while GAC removed some of the carboxylic fraction (from 35.9 to 29.1%). Formation potential of trihalomethanes (THMs) as compared to haloacetic acids formation potential (HAAFP) was highly influenced by HS. Higher yields of THMs resulted from chlorination of HS with a higher phenolic content and phenolic fraction in the HS gradually decreased from 60.5% to 15.8% through the water treatment. The structural and functional changes of HS were identified by elemental, Fourier-transform infrared (FT-IR) and proton nuclear magnetic resonance (¹H NMR) analyses, and these results were mutually consistent. The functional distribution data obtained by using A-21 resin could be used to support the interpretation of data obtained from the spectroscopic analyses. Decreases in ratio of UV absorbance at 253 nm and 203 nm (A_{253}/A_{203}) and DBPFPs/DOC showed consistent trends, therefore, A_{253}/A_{203} ratio may be a good indicator for the disinfection by-product formation potentials (DBPFPs).

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1. Introduction

A major problem occurred by natural organic matter (NOM) is the production of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). NOM including humic substances (HS) is widely known as a precursor of DBPs. NOM is partially removed in the conventional drinking water treatment process system such as coagulation/sedimentation and sand filtration. A plant can remove more NOM with additional water treatment processes to lower DBP levels before releasing the water to the distribution system. The chemical structure and compositions of NOM could be changed by physicochemical water treatment processes and the difference in NOM has been shown to cause changes in its reactivity with disinfectants [1,2].

HS in NOM are described as heterogeneous, polyfunctional polymers formed through the breakdown of plant and animal tissues and/or synthesis of products by chemical and biological processes [3]. HS are generally one-third to one-half of the dissolved organic carbon (DOC) in natural waters [3], and play an important role in the properties and functions of natural water systems. However, HS are still among the least understood and characterized components in the environment because of their complex polymeric properties. In a previous study, it was observed that the disinfection by-product formation potentials (DBPFPs) of humic fraction (i.e., HS) in natural surface water were significantly high compared to the DBPFPs by non-humic fraction [4]. Especially, specific molecular structure of HS has more effects on the formation of DBPs during reaction with disinfectants. Therefore, molecular structure of HS is one of the main characteristics to be studied for DBPs control. To understand the role of HS in water chemistry, it is often necessary to fractionate NOM. The composition of HS could be investigated by numerous methods including physicochemical fractionation and spectroscopic measurements. XAD resin

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method has been reported in many applications for fractionation of NOM [5,6]. Systematic fractionation of HS as a reactive component using the XAD resin is generally considered as the state-of-art method and used to estimate the behaviors and properties of HS in physicochemical water treatment processes [7,8]. In the various XAD resins, the most popular sorbent has been the XAD-8 resin at pre-adjusted acidity. However, the manufacture of the XAD-8 resin has been ceased some years ago and substituted by XAD-7HP since their technical specifications are quite close each other. According to Miyata et al. [9] the XAD-7HP resin has the same chemical structures as the XAD-8 resin (poly methyl methacrylate), but is more porous and has high surface area. XAD-7HP is non-ionic aliphatic acrylic polymer which derives its adsorptive properties from its patented macroporous structure, and is physically stable due to the macroporous structure. The method measuring the spectrum of HS using various spectroscopy such as Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR) has been accepted as an adequate way to estimate the humic properties [10,11].

It is generally accepted that formation of DBPs depends highly on the organic matter content, but there are many other factors such as organic matter composition and water treatment methods applied. The effect of characteristics of chemical structure of HS on DBP formation potentials was studied; however, these results were mainly related to studies conducted with HS isolated from distinct surface and ground waters [12,13]. It is important to understand the behaviors of HS in the process waters at real water treatment plant as well as to characterize HS from water source. Therefore, the main purposes of this study are to compare the physicochemical and structural characteristics of HS isolated from raw and process waters in advanced water treatment, and to investigate the relationships between the formation potential of DBPs and various characteristics of HS. Knowledge on the interactions of chlorine with HS as well as characteristics of HS is essential to establish optimal treatment strategy for DBPs control. Therefore, we attempted to estimate the characteristics of DBPs generated by the different properties of the HS in aqueous environment, to provide an indication of DBPFP by considering the spectroscopic characteristics of HS, and to understand the characteristics of HS, as main contributors for DBPs formation, influenced by physicochemical reactions in the advanced water treatment.

2. Materials and methods

The first phase of this study was to isolate NOM from raw and process waters into humic and non-humic fractions with XAD resin at the advanced water treatment demonstration plant being operated for 10 months. In the second phase of study, humic fraction (i.e., HS) obtained in the first phase was analyzed for distributions of apparent molecular weight (AMW) and functional groups using molecular sieves and a weak-base secondary amine resin. And then, HS samples were analyzed by Fourier-transform infrared (FT-IR) and proton nuclear magnetic resonance (^1H NMR) spectroscopy, and elemental analysis.

2.1. Demonstration plant

The demonstration plant was built in the Gueui Water Treatment Plant (GWTP) in Seoul, Korea. GWTP designed to treat 300,000 m³/day adopts conventional water treatment processes consisting of pre-chlorination, coagulation/sedimentation, sand filtration and chlorination, and uses Han River water as a water source. Commercial liquid poly-aluminum chloride (PACl, 17% Al₂O₃) solution was used as coagulant and optimal coagulant dosage based on turbidity removal was decided by jar-test. Injection of coagulant is achieved without any mechanical mixer dripping through perforated pipes running the full width of the mixing flume about 600 mm above the water surface and just upstream of the point of turbulence. The demonstration plant consisted of ozone and granular activated carbon (GAC) was operated to study feasibility of introducing advanced water treatment processes. Table 1 outlines the operational parameters for GWTP and the demonstration plant, and the quality of the raw water is shown in Table 2. This ozone/GAC process was optimized based on DOC removal efficiency and economical aspect, and designed to treat 40 m³/day of sand filtered water.

2.2. XAD-7HP resin cleaning

In this study, the XAD-7HP resin was cleaned using method proposed by Ma et al. [8]. After packing the XAD-7HP resin in a glass column (ID: 3 cm), the resin was rinsed with 0.5N NaOH. Then, the resin was flushed sequentially for 24 h each with methanol, acetonitrile and methanol. The first 300 mL effluent of each extraction solvent was discarded, and then the extraction solvent was recycled through the resin column. Lastly, the resin column was rinsed sequentially with distilled water, 0.1N NaOH, 0.1N HCl and distilled water to remove remaining impurities. The rinse of resin column was repeated until the DOC concentration of the effluent of final distilled water rinsing step become below 0.2 mg C/L.

2.3. Collection and isolation of NOM sample

The separate grab samples were collected three times to give the average characteristics of the different process waters. The pH of collected water from each sampling point was adjusted to 2 by hydrochloric acid after filtration with 0.45 μm membrane filter in the laboratory. In case of pre-chlorinated water, residual chlorine was quenched with sodium sulfite. NOM from various water samples was isolated and extracted using methods performed by Thurman and Malcolm [14]. Fig. 1 shows isolation methods of humic and non-humic fractions from water sample. A glass column was filled with XAD resin (Amberlite XAD-7HP, Rohm & Haas Co., PA, USA) up to 40 cm. About 20 L of each sample filtered was passed through the glass column with flow rate of 10–15 mL/min, and the effluent collected is termed the non-humic fraction. A 0.1N NaOH was used to extract HS (i.e., humic fraction) adsorbed in the resin bed. And then, Na⁺ ions in the solution were substituted with H⁺ using cationic exchange resin (Amberlite IRC-50, Rohm & Haas Co., PA, USA). Each fraction was analyzed for various physicochemical

Table 1
Operating parameters of GWTP and the advanced water treatment demonstration plant

Process	Parameters	Designed values	Residual chlorine
Pre-chlorination ^a	Retention time	21.4 min	0.5 mg/L
Chemical mixing ^b	Effective head	600 mm	–
	Retention time	1.6 min	–
Flocculation	Paddle type	3 stages (6 basins)	–
	Retention time	25.4 min	–
Sedimentation	Rectangular	6 basins	–
	Retention time	3.2 h	–
Sand filter	Bed	Sand 60 cm, gravel 35 cm	Below 0.01 mg/L
	Filtration velocity	189.4 m/day	
	Retention time	54.1 min	
Ozonation	Output	40 g/h	–
	Contacting	$L \times W \times H$: 1.7 m \times 0.3 m \times 5.5 m	
	Contact time	10 min	
	Ozone dose	1–1.5 mg/L	
	Residual ozone	0.05–0.1 mg/L	
GAC adsorption	Raw material	Bituminous coal type	–
	Particle size	0.9–1.1 mm (12 \times 40 mesh)	
	Effective size	0.65 mm	
	Uniformity coefficient	1.9 (Max.)	
	Apparent density	0.44 g/mL (Min.)	
	EBCT ^c	15 min	
	LV ^d	11 m/h	
	Bed volume	ID \times H: 450 mm \times 6 m	

^a Chlorine dosage in the pre-chlorination process = 2.5 mg/L.

^b PACl dosage in the coagulation process = 2.6 mg/L as Al₂O₃.

^c Empty bed contact time.

^d Line velocity.

characteristics. On the other hand, NOM samples before resin fractionation were filtered with 0.45 μ m membrane filter and molecular sieves (YM100, YM10 and YM1, Millipore Corp., USA) of 100 kDa, 10 kDa and 1 kDa to determine the distribution of apparent molecular weight (AMW).

2.4. Isolation of phenolic and carboxylic fractions

Using secondary amine weak-base [\sim N(CH₃)₂] resin (Amberlyst A-21, Rohm & Haas Co., PA, USA), HS were separated into two fractions, one which has higher content of phenolic functional groups and the other which has higher content of carboxylic functional groups [15]. The HS solution after passing through the resin column contains little phenolic functional groups by strong interaction between neutral nitrogen of the resin and the phenolic functional groups present in the HS solu-

tion at neutral pH. The content in the effluent collected is termed the carboxylic fraction and the isolation process is shown in Fig. 2.

2.5. Elemental, FT-IR and ¹H NMR analyses

HS powder obtained through freeze-drying HS solution substituted with H⁺ was analyzed for its structural and chemical characteristics. Elemental composition of HS was analyzed with an element analyzer (EA1108 CHNS/O Mode, Fisons Instrument, Italy). KBr (FT-IR Grade, Aldrich Co., USA) was mixed with HS in the ratio of about 100 to 1 and the IR spectra of the mixture were obtained by scanning it with IR spectrometer (Infinity Gold 60AR, Thermo Mattson, USA). An NMR analyzer (Avance 400, Bruker, Germany) was used to obtain the ¹H NMR spectra of HS. Approximately 50 mg of HS powder was added to 0.5 mL D₂O in a 10 mm NMR tube. The signal for D₂O was used as reference and set to 4.8 ppm chemical shift.

2.6. Analytical methods

DOC was determined with total organic carbon (TOC) analyzer (DC-180, Dohrmann, USA) after filtration of the samples with 0.45 μ m membrane filters. A UV-spectrophotometer (UV-2101PC, Shimadzu, Japan) was used to determine the absorbance at various wavelengths. For DBPFPs test, all

Table 2
The basic quality of the raw water in studied period

Date	October 2002–June 2003
Temperature (°C)	2.5–18.2
pH	6.8–7.9
Conductivity (μ s/cm)	152–186
Alkalinity (mg/L)	39–52
Turbidity (NTU)	2.4–7.5
DOC (mg/L)	1.82–2.53
UV ₂₅₄ (cm ⁻¹)	0.029–0.042

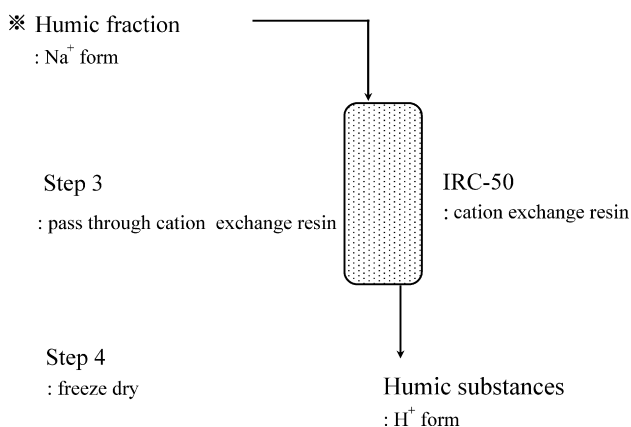
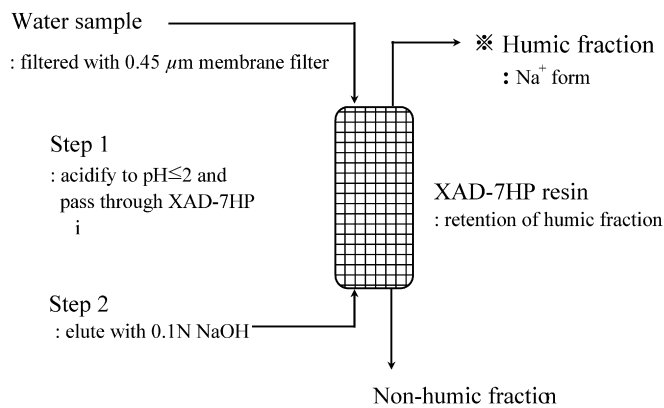


Fig. 1. Isolation methods of humic and non-humic fractions from water sample.

solutions were adjusted to pH 8 and were buffered with borate buffer solution. Chlorine was added as sodium hypochlorite at a dose of 3 mg $\text{Cl}_2/\text{mg C}$. Chlorinated samples were incubated at 20 °C for 48 h in headspace-free 300 mL amber bottles. At the end of the reaction period, residual chlorine was quenched with sodium sulfite (Na_2SO_3), and the concentration of DBPs was analyzed. The change in solution pH during the experiments was less than 0.2 units in all cases. In the cases of THMs, the 14 mL of each chlorinated and incubated sample was collected in 22-mL glass vial and sealed with aluminum sealing cap and

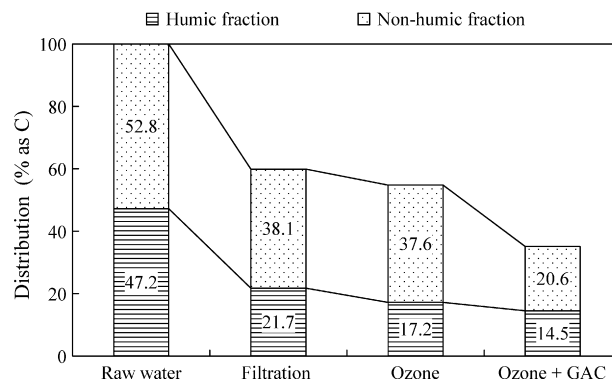


Fig. 3. Distribution of NOM isolated from raw and process waters at the demonstration plant.

Teflon-lined septa. The volatile compounds in samples were concentrated at headspace of the glass vial and injected into GC (HP-5890, Hewlett Packard, USA). Five HAAs were extracted with methyl *tertiary*-butyl ether (MtBE) and derivatized with acidic methanol. GC/MSD (3800CP, Varian, USA) was used to analyze for the HAAs by employing EPA Method 552.2 [16].

3. Results and discussion

3.1. Distribution of HS in water treatment processes

The variation of average distribution of humic and non-humic fractions in NOM during water treatment is shown in Fig. 3, and the average DOC decreased from 2.28 mg/L to 1.36 mg/L during conventional water treatment processes and decreased to 0.80 mg/L through ozonation and carbon adsorption. Humic and non-humic fractions decreased from 47.2% to 21.7% (from 1.08 to 0.49 mg C/L) and 52.8% to 38.1% (from 1.20 to 0.87 mg C/L), respectively, through conventional water treatment based on the content of raw water. Each NOM fraction decreased significantly during the conventional treatment processes including coagulation/sedimentation and filtration processes as shown in Fig. 3, since NOM even in soluble state might be removed by frequent contact of functional groups such as phenolic and carboxylic groups in dissolved organic molecules with coagulant and/or

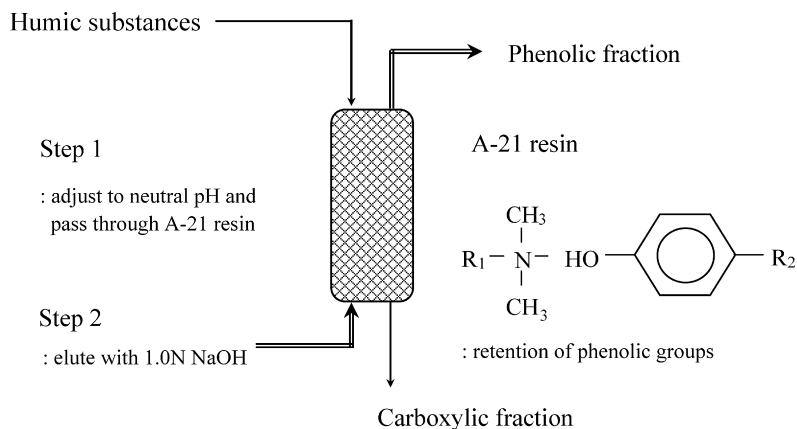


Fig. 2. Isolation process of carboxylic and phenolic fractions from humic substances (HS).

flocculant (i.e., various hydroxo-metallic complexes) detained in filter bed.

Through ozonation and carbon adsorption, the humic and non-humic fractions gradually decreased from 21.7% to 14.5% (from 0.49 mg C/L to 0.33 mg C/L) and from 38.1% to 20.6% (from 0.87 mg C/L to 0.47 mg C/L), respectively, as shown in Fig. 3. This result could possibly be explained due to increase in bioactivity on the carbon surface by 10 months operation. That is, biodegradation of NOM onto GAC and/or their sorption by the biofilm that developed on GAC is the principal mechanism for NOM removal. One of minor possibilities is that hydrophobicity of activated carbon surface might be reduced by hydrophilic oxygenated functional groups. Although all of the surface functional groups could not become hydrophilic, the adsorption capacity of non-humic fraction including hydrophilic compounds might be enhanced by increase in hydrophilic sites [17]. In any case, ozonation followed by activated carbon is effective process to reduce the non-humic fraction from conventionally treated water.

3.2. DBP formation potentials of HS

Since interpretation of absorbance data at only a single wavelength (e.g., 254 nm) fails to take advantage of the substantial information that must be embedded in the rest of the UV spectral data, ratio of UV absorbance at 253 nm and 203 nm (A_{253}/A_{203}) was proposed by Korshin et al. [18]. The ratio and DBPFs of HS isolated from the raw and process waters are plotted in Fig. 4(a). THMFP/DOC and HAAFP/DOC of HS isolated from raw water were 85.6 $\mu\text{g}/\text{mg C}$ and 20.2 $\mu\text{g}/\text{mg C}$, respectively. Through ozonation and carbon adsorption, these values were gradually decreased from 38.4 $\mu\text{g}/\text{mg C}$ to 24.8 $\mu\text{g}/\text{mg C}$ and from 13.8 $\mu\text{g}/\text{mg C}$ to 9.0 $\mu\text{g}/\text{mg C}$, respectively. The formation potential of THMs, compared to that of HAAs, was significantly high, since electrophilic reaction sites in the HS molecule mainly influence the formation of THMs. That is, THM formation was influenced by abundant reaction sites such as electrophilic structure and unsaturated bond in NOM molecule, compared to HAA formation. However, the THMFP/DOC decreased significantly through physicochemical water treatment, while specific reaction sites in HS for HAAs formation was not effectively reduced by the water treatment.

A_{253}/A_{203} ratio decreased from 0.160 to 0.102 by conventional water treatment processes as shown in Fig. 4(a). As A_{253}/A_{203} ratio gradually decreased from 0.102 to 0.055 by ozonation and carbon adsorption, DBPFs/HS decreased. The changes of A_{253}/A_{203} ratio of HS suggest that aromatic rings substituted with various functional groups in the HS molecules are structurally altered by physicochemical water treatment. A_{253}/A_{203} ratio is low for unsubstituted aromatic ring structures and increases for the aromatic rings highly substituted with hydroxyl, carbonyl, ester and carboxylic groups [18]. These functional groups are also considered to participate preferentially in the reactions generating DBPs. Decreases in A_{253}/A_{203} ratio and DBPFs/DOC showed consistent trends, and also the ratio A_{253}/A_{203} was as effective as UV_{254} (UV absorbance at 254 nm) to predict the formation potential of DBPs, as

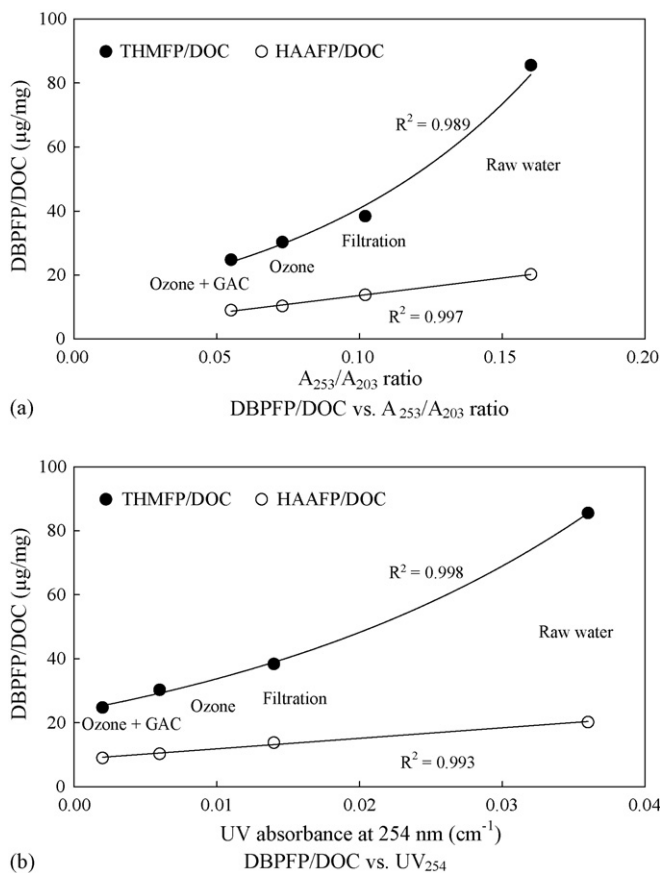


Fig. 4. Relationships between the DBPF and UV absorbance of HS solution: (a) DBPF/DOC vs. A_{253}/A_{203} ratio and (b) DBPF/DOC vs. UV_{254} .

shown in Fig. 4. Therefore, A_{253}/A_{203} ratio may be a good indicator of the tendency for the DBPs formation since the prediction of DBP formation through collection and interpretation of absorbance data at only a single wavelength (e.g., UV_{254}) may be limited by insufficient information in some cases.

3.3. Physicochemical and structural characteristics of HS

3.3.1. AMW distribution

Molecular weight distribution of HS obtained from raw and process waters was measured in term of DOC, and the results are shown in Fig. 5. The portion of organic matters in the range of 0.45 μm to 100 K and 100–10 K show 19.2% and 31.4%, respectively, in the raw water. The portion of organic matters below AMW 1 kDa showed 44.6%, which was gradually increased to 59.1% after ozonation. It is quite likely that ozone can transform large molecular weight organic matter to smaller one through partial oxidation of organic matter. HS of smaller molecular weight is considered to contain less specific reaction sites. Therefore, DBPFs of HS would be decreased with not only reduction of organic matter above AMW 10 kDa but also reduction of specific reaction sites. Consequently, both ozone and chlorine react as electrophilic oxidants on the same sites including DBP precursors such as phenols. Moreover, it was possible that decrease in DBPFs might be attributed to

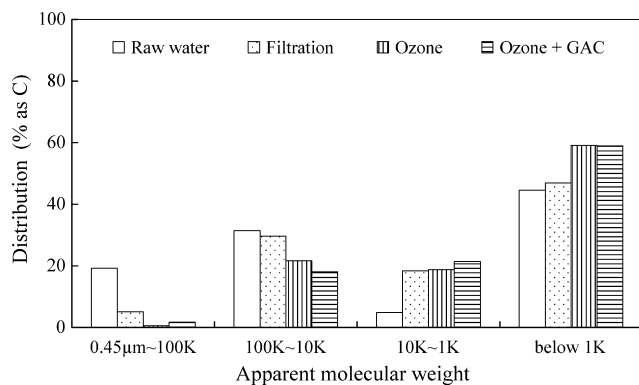


Fig. 5. Variation in molecular weight of HS isolated from raw and process waters.

depolymerization of HS. Therefore, the use of ozone before chlorine could reduce the formation of DBPs.

3.3.2. Distribution of functional groups

The variation of distribution of phenolic and carboxylic fractions in HS through water treatment process is shown in Fig. 6. Relative content of phenolic and carboxylic fractions decreased from 60.5% to 24.3% and 39.5% to 29.1%, respectively, through conventional water treatment based on the content in HS isolated from raw water. Phenolic fraction decreased by 36.2% through conventional treatment processes while the carboxylic fraction decreased by only 0.4%. As shown in Fig. 4(a), this suggests the reduction in A_{253}/A_{203} ratio from 0.16 to 0.102 after conventional treatment processes was solely due to the removal of phenolic fraction. That is, A_{253}/A_{203} ratio depends more on the content of phenolic fraction than that of carboxylic fraction in the HS. Moreover, higher formation potential of DBPs resulted from HS with higher phenolic content. This result was consistent with the former study, which showed the aromatic phenolics from model compounds produced larger amount of DBPs [12]. Compounds with hydroxyl (–OH) functional groups had both high halogen consumption and haloform formation, whereas compounds attached with carboxyl (–COOH) functional groups had lower halogen consumption and haloform formation [19]. In addition, it was recognized that the content and substitution type of phenolic ring structure in the HS molecule highly influenced DBPs

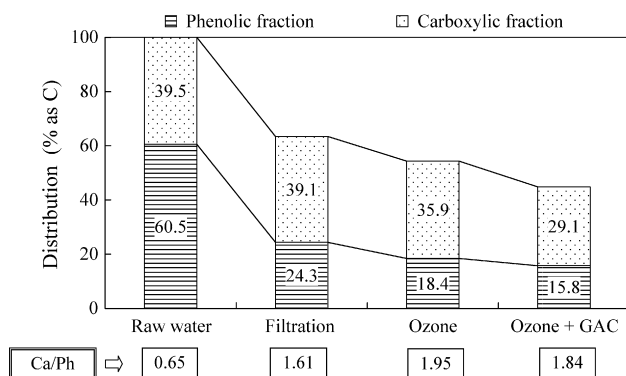


Fig. 6. The distribution and ratio of carboxylic fraction to phenolic fraction (Ca/Ph) in HS.

Table 3

Elemental composition and molar ratios for humic substances (HS) extracted from the water samples

Sample	Elemental composition (wt.%)					Molar ratio		
	C	H	N	O	S	H/C	N/C	O/C
Raw water	46.60	5.46	0.81	47.13	ND ^a	1.406	0.015	0.759
Filtration	44.85	5.27	0.45	49.43	ND ^a	1.409	0.009	0.827
Ozone	39.67	4.95	0.21	55.18	ND ^a	1.496	0.004	1.043
Ozone/GAC	41.75	5.16	0.20	52.89	ND ^a	1.485	0.004	0.950

^a Not detected.

formation. For ozone followed by GAC, ozone oxidizes the phenolic fraction (from 24.3 to 18.4%), whereas GAC removed less of the phenolic fraction (from 18.4 to 15.8%). Alternatively, ratio of carboxylic fraction to phenolic fraction (Ca/Ph) in HS increased through ozonation, and after this ratio was decreased by GAC treatment because GAC removed some of the carboxylic fraction (from 35.9 to 29.1%) rather than phenolic fraction.

3.3.3. Elemental composition

The elemental compositions of the humic materials and molar ratios calculated from the elemental analyses are given in Table 3. Molar ratios such as H/C, O/C, and N/C obtained by elemental analyses may provide valuable information on composition of HS. For example, H/C ratio was around 1.0, which is considered to indicate mature HS in most soil and water and implies a chemical structure consisting predominantly of aromatic framework [20]. Therefore, the ratio could increase with decreasing humification (i.e., condensation) degree [21]. The results of elemental analysis for HS extracted from raw and process waters were compared. The molar ratio of H/C increased by ozonation rather than conventional water treatment processes, indicating the increasing aliphatic carbon compared to aromatic carbon. Also, the N/C ratio decreased through water treatment, while the O/C ratio increased except for after carbon adsorption. This indicates a relatively high content of carboxylic groups in HS, and was consistent with the result of increasing or decreasing Ca/Ph ratio obtained from the isolation of phenolic and carboxylic fraction using A-21 resin.

3.3.4. FT-IR spectra

The IR spectra of the HS extracted from the raw and process waters are shown in Fig. 7 and these spectra mainly show the existence of oxygen-containing functional groups. The mass of powdered HS sample for each FT-IR analysis was not exactly same each other; thus, the absorbance values in the y-axis were not provided. Interpretation of the absorption bands of HS was done as described in the literature [22,23]. The band at around 3400 cm^{-1} is generally attributed to OH groups and bands at $2995\text{--}2965\text{ cm}^{-1}$ are assigned to C–H, C–H₂ and C–H₃ stretching of the aliphatic groups. The bands at $1646\text{--}1640\text{ cm}^{-1}$ and $1560\text{--}1551\text{ cm}^{-1}$ are attributed to C=O stretching vibration of carboxylic acids and ketones/quinones, respectively. The bands at around 1450 cm^{-1} and 1410 cm^{-1} are attributed to C–H deformation of aliphatic and CH₃ groups, respectively. Also, bands in the $1280\text{--}1137\text{ cm}^{-1}$ region are attributed to C–O stretch-

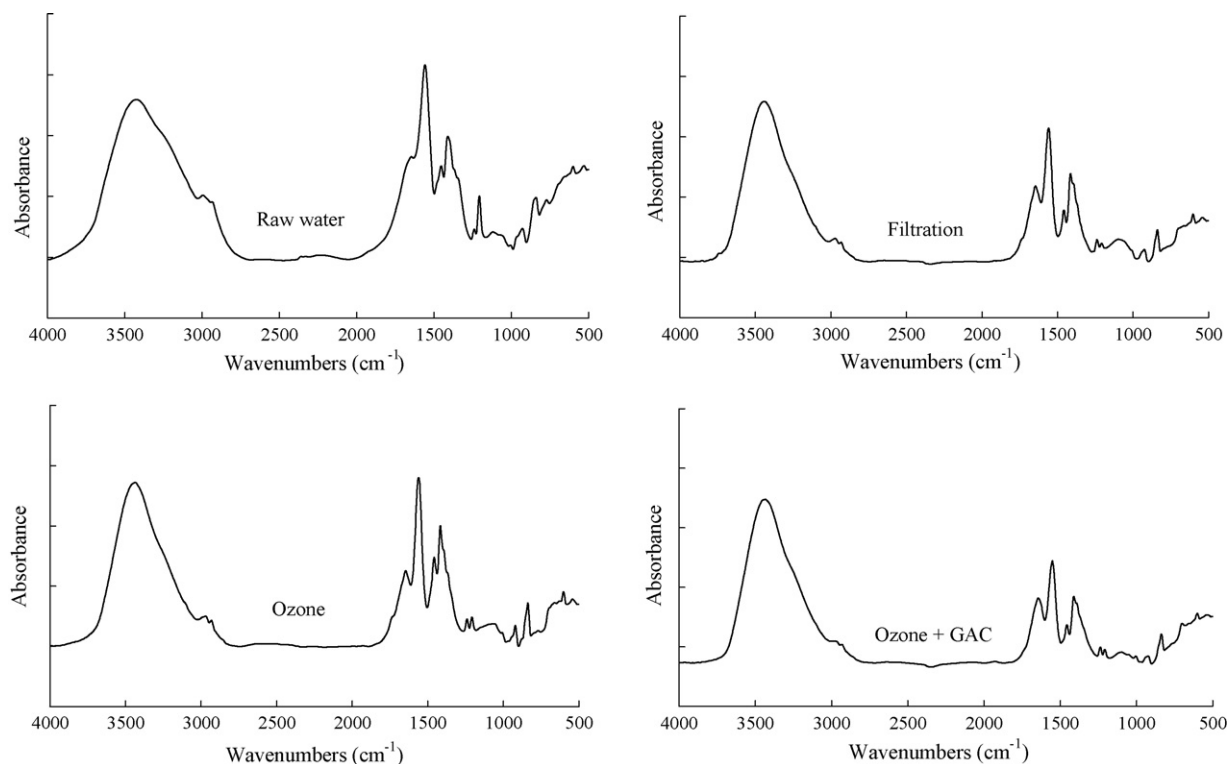


Fig. 7. FT-IR spectra of isolated HS from raw and process waters.

ing of esters, ethers and phenols, and band at around 830 cm^{-1} can be assigned to OH stretching vibration of carboxylic groups.

From this result, the peak area of $1560\text{--}1551\text{ cm}^{-1}$ decreased by conventional treatment, indicating cyclic and/or alicyclic compounds were removed. And also, the peak area of $1560\text{--}1551\text{ cm}^{-1}$ and $1450\text{--}1410\text{ cm}^{-1}$ slightly increased by ozonation, while these peak area decreased by carbon adsorption and/or biodegradation. It suggests that portion of cyclic compounds in the HS decreased by coagulation/filtration process and aliphatic groups slightly increased by ozonation. Therefore, the aliphatic compounds and ketones were mainly adsorbed and/or biodegraded by activated carbon. The structural changes of HS through water treatment processes were consistent with the result from the ^1H NMR spectra.

3.3.5. ^1H NMR spectra

^1H NMR spectra were obtained for basic structural information of HS. General assignments for the four major regions of the proton spectra are as follows: (1) $0\text{--}1.6$ ppm, protons on methyl and methylene carbons directly bonded to other carbons; (2) $1.6\text{--}3.2$ ppm, protons on methyl and methylene carbons alpha to aromatic rings, carboxyl, and carbonyl groups; (3) $3.2\text{--}4.3$ ppm, protons on methyl, methylene, or methyne carbons directly bonded to oxygen or nitrogen, including carbohydrate and amino acid protons; (4) $6.0\text{--}8.5$ ppm, protons attached to unsaturated carbons and aromatic protons [8]. For a more effective comparison, each spectrum was quantitatively analyzed in accordance with literature results of assignments for the chemical shift in ^1H NMR spectra as shown in Table 4.

Percentage of the region III ($3.2\text{--}4.3$ ppm) including olefin and acetylene compounds decreased through ozonation, while percentage of the region IV ($6.0\text{--}8.5$ ppm) including aromatic compounds decreased through conventional water treatment processes including pre-chlorination, coagulation/sedimentation and filtration. Less reduction of region IV by ozonation was due to the reduction of specific reaction sites during conventional water treatment. That is, since specific reaction sites such as aromatic ring structures in the HS molecule were already attacked by chlorine through pre-chlorination in conventional water treatment process, specific reaction sites to react with ozone or OH radical through ozonation were already

Table 4
 ^1H NMR chemical shift regions and their relative contributions

Chemical shift region (ppm)	Relative contributions (%)			
	Raw water	Filtration	Ozone	Ozone/GAC
I ($0.0\text{--}1.6$) ^a	38.6	41.3	46.6	44.7
II ($1.6\text{--}3.2$) ^b	37.0	39.0	38.7	38.7
III ($3.2\text{--}4.3$) ^c	11.3	10.9	6.1	6.3
IV ($6.0\text{--}8.5$) ^d	13.1	8.8	8.7	10.3
$P_{\text{Al}}/P_{\text{Ar}}$ ratio ^e	5.8	9.1	9.8	8.1

^a Aliphatic methyl and methylene.

^b Protons of the methyl and methylene groups α to aromatic rings, protons on carbons in α position to carbonyl, carboxylic acid, ester, or amino acid.

^c Protons on carbon of hydroxyl, ester and ether, and protons on methyl, methylene, and methyne carbons directly bonded to oxygen and nitrogen.

^d Aromatic protons including quinones, phenols, oxygen-containing heteroaromatics.

^e The ratio of aliphatic protons to aromatic protons (regions I and II/region IV).

reduced. However, other unsaturated sites such as olefin and acetylene bonds were directly or indirectly oxidized by ozonation. The ratio of aliphatic to aromatic protons (P_{Al}/P_{Ar}) was increased from 5.8 to 9.1 by conventional water treatment system as shown in Table 4. This ratio increased by ozonation, while it was decreased due to reduction of aliphatic groups through carbon adsorption and/or biodegradation. Percentage of the region IV relatively increased after GAC, since aliphatic groups in the HS could be selectively adsorbed and/or biodegraded to activated carbon. These results were mostly consistent with the result from FT-IR spectra of the HS.

4. Summary and conclusions

Through conventional water treatment processes, humic fraction was more reduced than non-humic fraction and phenolic fraction was mainly removed compared to carboxylic fraction. It was found that ozone can decrease the humic fraction, whereas GAC can remove the non-humic fractions in conventionally treated water through selective adsorption and/or biodegradation. FT-IR and ^1H NMR were employed for characterization of HS isolated from raw and process waters at the advanced water treatment plant. The reduction of aromaticity and humification degree was identified by these spectroscopic analyses.

The HS influenced largely the formation of THMs rather than HAAFP, and also a higher yield of THMs resulted from chlorination of HS with a higher phenolic content. DBP formation potentials decreased by breakdown of large molecular weight HS as well as reduction in aromaticity of HS molecule through the water treatment. However, amount and species of DBPs produced were more influenced by chemical and structural characteristics such as hydrophobicity and functionality rather than mere breakdown of organic matter. The preferential removals of the HS caused the change in A_{253}/A_{203} ratio; therefore, A_{253}/A_{203} ratio may be a good indicator for changes in reactivity of the NOM with chlorine. The formation of DBPs may be predicted by monitoring A_{253}/A_{203} ratio, a relatively simple measurement.

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