

SPECTROSCOPIC CHARACTERIZATION OF DISSOLVED ORGANIC MATTER AND DBPS FORMATION POTENTIALS IN A PILOT-SCALE ADVANCED WATER TREATMENT FACILITY

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I. INTRODUCTION

Traditional water treatments, such as coagulation and sand filtration, are limited for removing micro pollutants, refractory organic matters or disinfection by-products (DBPs) precursors. Advanced water treatments, however, have been targeted at controlling them. The most preferred methods for these are known as granular activated carbon (GAC) adsorption and ozone processes. Although it is well known that the quantity and the quality of DOM undergo substantial changes in the conventional drinking water treatment, there is still a possibility of the changes in DOM with the advanced treatment. Such changes may also affect DBPs formation potentials. Recently, fluorescence measurements have been widely used to better understand different DOM components and the dynamics because it is easy to use with minimal pretreatment of samples and it is very sensitive compared to UV-vis spectroscopy. The objective of this study is to compare DOM fluorescence characteristics and DBPs formation potentials in GAC adsorption and ozone oxidation processes at a pilot scale plant.

II. MATERIALS & METHODS

In this study, post-sand filtration samples were taken once a week, in volumes of 1L for 9 weeks from an advanced water treatment pilot plant near Seoul in Korea. This sample was used as a reference to compare the change of DOM properties with the samples treated by different advanced treatments. Two main processes were compared as follows.

Process 1) Treated water from coagulation and sand filtration → Ozone oxidation → GAC adsorption (GAC1).

Process 2) Treated water from coagulation and sand filtration → GAC adsorption (GAC2).

All samples were filtered through a pre-ashed GF/F filter (0.7 μ m) prior to further analyses. The concentrations of dissolved organic carbon (DOC) were analyzed using a TOC analyzer (SHIMADZU TOC-V CPH) equipped with a high sensitivity catalyst. A UV-vis spectrometer (HACH, DR5000) was used to measure UV absorbance at a wavelength of 254nm (UV₂₅₄). Fluorescence measurements were made in a Perkin-Elmer (LS-55). To maintain a constant fluorescence measurement and equipment conditions, 10 μ l/l of quinine sulfate dehydrate in 0.05M H₂SO₄ solvent was prepared and used for a standardized fluorescence intensity (units of quinine sulfate equivalents, QSE) [1]. Fluorescence excitation-emission matrix (EEM) was measured at the

excitation wavelengths from 220 nm to 500 nm and emission wavelengths from 280 nm to 550 nm. PARAFAC modeling was used for total 36 EEMs analysis that were implemented using the MATLAB 7.0 with DOMFluor toolbox [2, 3]. Analysis of trihalomethane and haloacetic acid were based on the procedures described by US EPA methods (552.2) and standard methods (5710B, 6232B and 6215B) [4].

III. RESULTS & DISCUSSION

A. Changes in concentration of dissolved organic carbon (DOC) after the processes.

For the process 1, our results showed that the DOC concentrations of the influent samples (i.e. the samples after sand filtration) were 0.8 \pm 0.2 mgC/l. The concentrations were decreased, ranging from 0.8 \pm 0.2 to 0.7 \pm 0.2 mgC/l after the ozone process and they were further decreased after an additional treatment of GAC adsorption (GAC1), ranging from 0.7 \pm 0.2 to 0.4 \pm 0.1 mgC/l after GAC1. The removal rates of DOC 10.6 \pm 2.3% and 48.6 \pm 11.5% during the ozone oxidation and during GAC adsorption. The final DOC removal rate was 54.2 \pm 9.3%. For the process 2, DOC concentrations of the influent samples were equal to the process 1, ranging from 0.8 \pm 0.2 to 0.6 \pm 0.2 mgC/l after GAC2 and the final DOC removal rate was 51.6 \pm 13.6%.

B. Changes of SUVA values with the processes.

For the process 1, our results showed that the SUVA value of the influent samples were 2.2 \pm 0.4 l/mgC-m. They were decreased after the ozone process, ranging from 2.2 \pm 0.4 to 1.3 \pm 0.4 l/mgC-m. The reduction may be attributed to the destruction of relatively high molecular weight aromatic structures by the oxidation (Park et al., 2007). In contrast, they were slightly increased after GAC adsorption, ranging from 1.3 \pm 0.4 to 1.6 \pm 0.3 l/mgC-m after GAC1. For the process 2, the SUVA values were ranging from 2.2 \pm 0.4 to 1.8 \pm 0.4 l/mgC-m after GAC2 (Table 1).

C. Changes of fluorescence characteristics with the processes.

Three fluorescence components (C1, C2 and C3) were identified using PARAFAC. Component 1 (C1) had the maximum excitation/emission (ex/em) at 360-400 nm/454.5-494 nm, showing humic-like fluorescence characteristics. Component 2 (C2) exhibited the maximum ex/em at 325-350 nm/416-436 nm, resembling a typical aquatic fulvic acid (fulvic-like fluorescence). Component 3 (C3) had the maximum ex/em at 260-305 nm/ 322-384.5 nm, showing protein-like fluorescence characteristics. The

maximum fluorescence intensity (F_{max}) of C1 was slightly decreased after the ozone process. %C1, %C2 and %C3 for PARAFAC removal rates were the most efficient at ozone-GAC1 87.2±3.2%, 81.1±15.0 % and 82.0±22.2%, respectively.

TABLE I. DOC, SUVA, and fluorescence PARAFAC peak intensities of the samples before and after treatments.

	DOC (mgC/l)	SUVA (l/mgCm)	Fluorescence PARAFAC peak intensities (QSE)		
			C1	C2	C3
Influent	0.8±0.2	2.2±0.4	15.0±3.6	7.5±3.4	4.7±7.1
Ozone	0.7±0.2	1.3±0.4	3.1±1.0	1.7±0.4	1.7±1.8
GAC1	0.4±0.1	1.6±0.3	1.9±0.5	1.4±0.8	1.0±1.2
GAC2	0.6±0.2	1.8±0.4	6.4±1.4	3.0±1.2	2.3±2.4

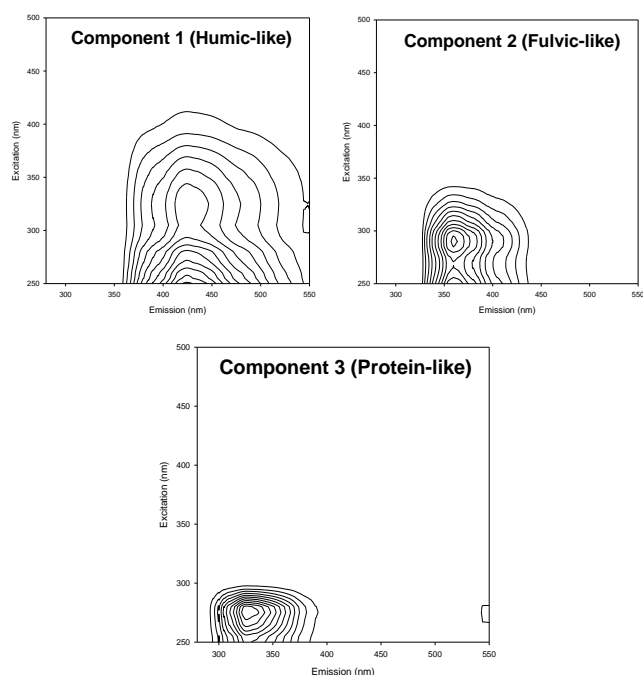


Fig. 1. Fluorescence PARAFAC components.

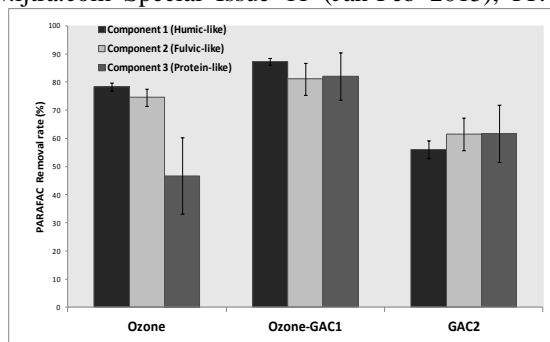
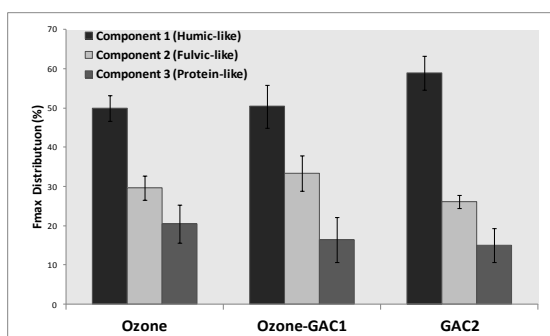


Fig. 2. F_{max} distributions and removal rates of PARAFAC after treatment processes.

IV. CONCLUSIONS

- 1) Both SUVA values and %C1 were substantially reduced after ozone treatment, suggesting the preferential removal of high molecular aromatic structures by the processes.
- 2) The greater extent of the increase was found in the SUVA values for GAC adsorption than the ozone process, suggesting the preferential removal of smaller sized DOM molecules by GAC.
- 3) More efficient removal was found for C1(humic-like) after ozone versus GAC processes, while the opposite trend, for C3 (protein-like).

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