Fluorescence Excitation-Emission and PARAFAC to monitor natural organic matter change in pilot scale UV/H_2O_2-GAC process

S.H. Nam[1], J.W. Koo[1], E.J. Kim[1], T.M. Hwang[1,†]

[1] Korea Institute of Civil Engineering and Building Technology, 283 Goyangdar-Ro, Ilsan-Gu, Goyang-Si, Gyeonggi-Do 411-712, Republic of Korea
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Presenting author email: taemun@kict.re.kr

Introduction

Due to the recent abnormal climate change, the average temperature of river and lake water has increased. Further, substances having taste and odor due to the presence of algae are detected even in the winter. In particular, natural organic matter (NOM), which is the major component of natural colloidal matter, is a major concern for a drinking water treatment. The understanding of NOM's structural chemistry can be used for the design of a treatment process for eliminating these components as well as their removal from drinking water (Leenheer, *et al.*, 2003). The quantitative and qualitative understanding of the chemical properties and reactivity of NOM provides valuable information for a drinking water treatment (Kavurmaci, *et al.*, 2016). In this study, the changes in NOM were observed by operating an advanced oxidation technology (AOP) process. This specialized process had recently been introduced for the effective removal of the emerging contaminants, which include substances having taste and odor, residual pharmaceuticals, non-biodegradable materials (including flame retardant materials), and chlorine-resistant pathogenic microorganisms through conventional water treatment processes. The purpose of this study is to analysis the natural organic substance change with fluorescence excitation emission matrix coupled with parallel factors analysis (PARAFAC) (Yu, *et al.*, 2010). Especially, this study focuses on the impacts of UV alone and UV AOP consisting UV/H_2O_2 on organic matter characteristics prior GAC process.

Methods

Pilot scale experiments with UV AOP/GAC process were carried out onsite at N drinking water facility in I city. The UV process operates in two type models which low pressure UV is applied in line 1 and medium pressure UV is applied in line 2. These pilot systems comparatively evaluate the oxidation potential according to the pre-treated waters that are treated by sedimentation or sand filtration process. The pilot plant has a capacity of 2,000 m^3/day, the UV dose was varied as 0 ~ 10 mg/L, the UV dose as 300~1000 mJ/cm^2. Fig. 1 shows the schematic process diagram and field picture. Fluorescence EEMs and absorbance spectra were analyzed using an Aqualog (HORIBA Instruments Inc.) from 240-550 nm using 2 nm for excitation intervals and 246.28-828.25 nm using 4.66 nm for emission using a medium gain and 1.5 s integration for emission detection. Fluorescence EEM data were analyzed using the PARAFAC algorithm within the Eigenvector Inc. Solo Package.

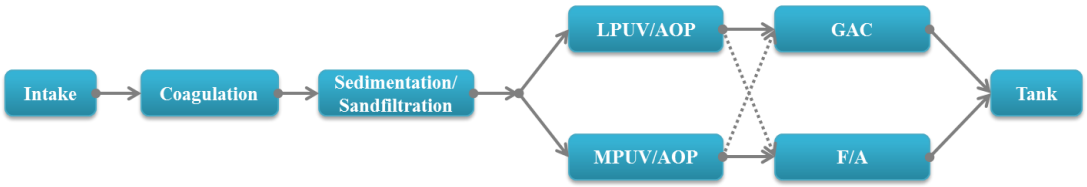

Fig. 1. Schematics of UV/AOP pilot plant

Results and Discussion

The PARAFAC analysis was conducted using 50 F-EEMs water samples obtained from the operation of the drinking water treatment. Based on the PARAFAC analysis, two optimum models were determined. The outlier of the data was eliminated in order to facilitate the modelling process as well as the model validation using a split-half method. The model accounted for 85.3% of the variance. The split-half validation match was 88.6% and the core consistency was 84%. The C1 component is explained by protein-like fluorophores. The C2 component constitutes terrestrial humic-like fluorophores when compared to the components identified in previous research. The generated model was split-half validated. To evaluate the quantitative changes of EEMs, the PARAFAC analysis was applied to all the samples. The concentration loadings for the major components were then analyzed.

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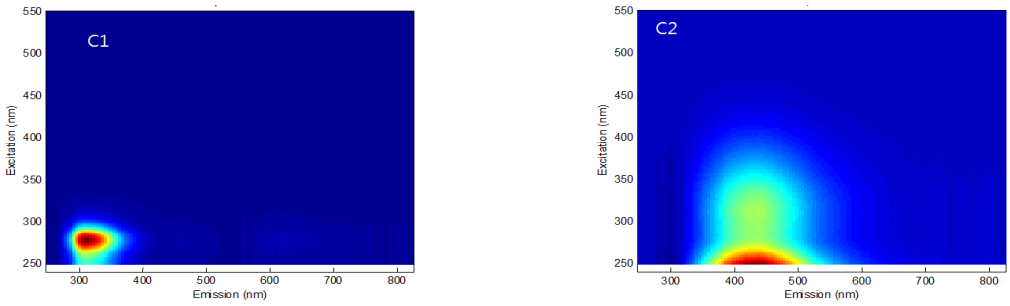

(a) (b)

Fig. 2. Excitation-emission contours for PARAFAC model components C1 (a) and C2 (b)

Fig. 3 compares the normalized PARAFAC concentration loadings for the two components of the sample. The concentration loadings are expressed for each process in the drinking water treatment operated by the UV process. The UV dose for MPUV and LPUV was 500 mJ/cm^2. The main component of the raw water was found to be Component 2. The comparison of MPUV and LPUV indicated that Component 2 was barely removed, and its removal occurred in the F/A and GAC processes. Component 1 was not removed in the MPUV and LPUV processes, and it was also barely removed in the F/A and GAC processes. The removal of Component 2 (i.e., humic-like fluorescence) was effective in the adsorption process.

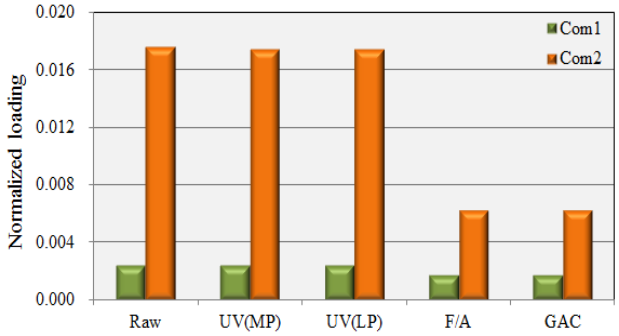

Fig. 3. Normalized concentration PARAFAC loadings for C1 and C2 for the drinking water treatment

Conclusions

In this study, the number of fluorescence components for the drinking water treatment could be identified through a PARAFAC model. In the target process of this study, the number of components was found to be two, and the changes in the components for each process could be observed. In particular, Component 1 [i.e., tryptophan-like substances (protein-like)] was removed in the UV/H_2O_2 process. Component 2 (Terrestrial humic-like) was mostly removed in the adsorption process. Therefore, the changes in the characteristics of organic matter for each process could be observed through the PARAFAC model. A more accurate PARAFAC model can be obtained if more data are additionally secured. Additional research is currently in progress. The organic substance monitoring technology based on fluorescence spectroscopy may be used as an effective tool for characterizing structural changes of organic substances and evaluating the removal efficiency of AOP.

References

[1] Leenheer, J. A. and Croue´J. P. (2003) Peer reviewed: Characterizing aquatic dissolved organic matter, Environ. Sci. Technol., 37, 18A–26A.

[2] Kavurmaci, S, S., Birben, N. C., Tomruk, A. and Bekbolet, M. (2016) Characterization of organic matter in natural waters by EEM fluorescence properties, Desalination and Water Treatment, 57, 2428–2436.

[3] Yu, G. H., He, P. J., Shao, L. M. (2010) Novel insights into sludge dewaterability by fluorescence excitation–emission matrix combined with parallel factor analysis, Water Res., 44, 797–806.

Acknowledgements

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