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THE DIVERGENCES OF ORGANIC CHARACTERISTICS OF SOURCE WATERS FROM FS AND CCL WATER TREATMENT AND ITS REMOVAL BY ALUM

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Abstract

Few papers were well discussed about whether the variation of organic property and initial turbidity could affect its removal by coagulation. In this study, EEFMs(Excitation Emission Fluorescent matrix) of DOM (Dissolved organic matter) by parallel factor analysis (PARAFAC) was applied to elucidate the variation of organic matter in both source waters of FS and CCL water treatments. Meanwhile, the molecular weight cut-offs was measured by HPLC equipped with Diode Array Detector (DAD) containing of HPSEC column. Current finding reveals that both source waters containing of four major fluorescent components were varied with the change of seasons. MWCOs were also affected by the change of low flow and flooding season. The optimal alum dosage was simultaneously affected by the initial turbidity as well as organic characteristic. Interestingly, the aggregation of lower or higher MWCOs was found in high alum dosage added.

Keywords

Excitation Emission Fluorescent Matrix (EEFM); Parallel Factor Analysis (PARAFAC); Molecular Weight Cut-Offs; Alum

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1. Introduction

Dissolved organic matter (DOM) is a heterogeneous mixture of organic compounds in water bodies. It is composed of myriads of organic compounds which play pivotal ecological and biogeochemical roles in the environment (Wang et al., 2014; Findlay and Sinsabaugh, 2003; Hansell and Carlson, 2002). Fluorescence excitation-emission matrix (EEFM) combined with parallel factor analysis (EEFM-PARAFAC) has become a popular tool for probing the fate of DOM and understanding its environmental behaviors in natural and engineered systems (Borisover et al., 2009; Ishii and Boyer, 2012; Stedmon et al., 2003; Yang et al., 2015). PARAFAC modeling makes it possible to extract dissimilar fluorescent components with minimum residuals from a given EEFM dataset (Stedmon et al., 2003).

The coagulation–flocculation process is an important treatment technology with a wide range of applications in water and wastewater treatment facilities (Zheng et al, 2011). Four underlying components extracted from the EEFMs of DOM by parallel factor analysis (PARAFAC) were humic acid-like (A), fulvic acid-like (B), protein-like (C) and unidentified component (D), while the Missouri River DOM was dominated by A, B and C. Flocculation was effective for the hydrophobic organic compound A followed by the hydrophilic organic compounds B and C, whereas the smallest molecular size compound C was hard to treat (Zhu et al., 2014).

Fluorescence excitation–emission matrix spectros copy (EEFMs) for DOM characterization in flocculation process at present is not well known. Furthermore, few papers were well discussed about whether the variation of organic property and initial turbidity could affect its removal by coagulation. Of course, the change of molecular weight after coagulation was also worth analyzing. Hence, in this study, EEFM and molecular weight cut-offs of both reservoirs, including CCL and FS in the southern Taiwan, were respectively employed to characterize DOM removal by the coagulation process.

2. Materials and Methods

2.1 Source Waters and Coagulant Preparation

CCL and FS water treatment, located at southern Taiwan, includes a series of purification processes. Source water of CCL water treatment came from reservoir pumped from Gaoping River. Regarding to source water of FS water treatment, it directly pumped from Gaoping River. Finished water treated from both treatments provides high quality of drink water for residents living in Kaohsiung city where the second metropolis in Taiwan is. Samples of both source water samples were collected during March and June in 2015.

The coagulant solution (100 mg/L aluminum sulphate) [$Al_2(SO_4)_3 \cdot 18H_2O$ from J.T. Baker] was prepared as stock solution. Each runs of jar test were respectively filled with 1 L of source water measured with a graduated cylinder. The coagulant dose added to each jar was carefully measured with a burette for controlling the concentration of coagulant to reach the range of aluminum ions of 0-1.5 mg /L. Addition of coagulant was followed by 3 min of rapid mixing at 100 rpm, flocculation for 15 min at 35 rpm and 30 min of settling. Then, water samples pumped by pipette at constant depth in jar beaker were filtered through 0.45 μm membrane filter (Mixed cellulose ester, Advantec MFS Inc., USA). Filtered samples were analyzed with EEFM, residual turbidity and molecular weight cut-offs.

2.2 Analytical Parameters

2.2.1 EEFM (Excitation Emission Fluorescent Matrix) + PARAFAC

Regarding to the organic characteristic of water samples, fluorescent spectrometry (F-4500, Hitachi, Japan) was applied in this research. Whole samples must be filtered by 0.45 μm membrane filter (Mixed cellulose ester, Advantec MFS Inc., USA) before fluorescent measurement. EEFMs of whole samples were obtained by deducting from the background signal of pure water. PARAFAC is a statistical tool to decompose complex mixtures of DOM fluorophores in EEFM into non-co-varying components. The whole samples were measured with an excitation range of 200–450 nm (every 2 nm) and an emission range of 250–550 nm (every 3 nm). Inserting zero instead of missing values in parts of the data area could help PARAFAC quickly converge, leading to solutions having physical and chemical significance. PARAFAC modeling was accomplished through the use of DOMFluor Toolbox written by Stedmon& Bro (http://www.models.life.ku.dk/al_DOMFluor). Both programs are subroutines for the MATLAB R2010a. The three-way PARAFAC model was fitted for the entire dataset as a whole. Single value decomposition (SVD) was used for the initialization of loadings for the initial model. Analysis was performed for a PARAFAC model of the data to determine the correct numbers of factor (Thygesen et al., 2004).

2.2.2 Molecular Weights Cut-Offs (MWCOs)

HPLC (L-7100, Hitach, Japan) system equipped with Diode Array Detector (DAD) was used to measure the molecular weight of dissolved organic matter filtered by 0.45 μm membrane filter. Related operational condition and Integrated areas of different MWCOs operated by Peak-fit software was modified by the report of Chow et al.(2008).

2.2.3 Turbidity

Turbidity was analyzed by turbidity meter (TN100, EUTECH, FRG) in according with the standard of EPA method in Taiwan.

3. Results and Discussion

3.1 Organic Characteristics of Both Source Waters

Regarding to the organic characteristics of source water in CCL water treatment, four components with varied EX/EM locations were appeared in different months, as shown in Fig.1 A. On March, 2015 (Fig1.A-1), four major components were in order of the percentage of fluorescent intensity 39% of 228,300/400 nm, 36% of 258, 308/412 nm, 13% of 248/448 nm, and 12% of 258/301 nm. On June, 2015(Fig.1 A-2), 220/276 nm (58%) was dominant organic. On September, 2015 (Fig.A1-3), the summation of percentage of fluorescent intensity for 220,276/300 nm (37%), and 258,308/400 nm (25%), was over 60% with similar trend of organic matter on Dec. 2015. For FS source water (Fig.1 B), four major components were also appeared in whole samples. Four major component were respectively appeared in different seasons, 240/440 nm (36%), 224,274/300 nm (21%), 260/450 nm (22%) and 246/480 nm (22%) on March; 220,276/300 nm (41%), 258,308/400 nm (36%), 270/457 (22%), and 240/454 nm (1%) on June; 224/300,260 (32%), 228/300,400 nm (28%), 272/480 nm (21%) and 320/420 nm(20%); 224/300 nm (32%), 240,300/410 nm (25%), 226/340 (24%) and 260/466 nm on Nov. in 2015.Apparently, the organic fluorescent components were varied with the change of seasons.

Pertaining to the variation of MWCOS for both source waters, the results of four times were shown in Fig.2. Similar molecular weight cut-offs with closed signal intensity were respectively found in < 1 k Da and 2 k Da on Sep., and 14 k Da and 50 k Da on Nov., 2015. Interestingly, similar molecular weight cut-offs, <1 k Da and 16 k Da, were still found in both source waters on June in 2015; however, the signal intensities were significantly different, which of CCL was higher than that of FS. On March, 2015, the locations of molecular weight cut-offs and signal intensity were different where 39 k Da of FS and 63 k Da of CCL were respectively appeared. Observed from the changes of molecular weight cut-offs on June and Sep, this may be related with the variations of low water and flooding seasons in Taiwan.

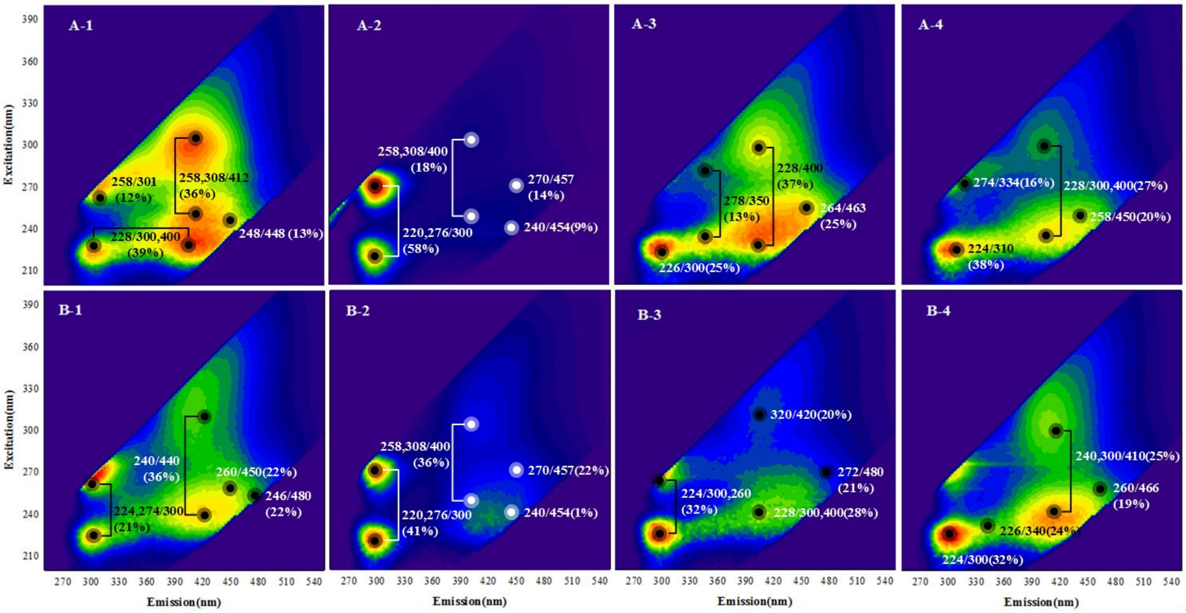

Figure 1: *Major components of DOC using EEFM+PARAFAC for (A) CCL (B)FS source water on (1) March (2) June (3) Sep. (4) Nov. in 2015*

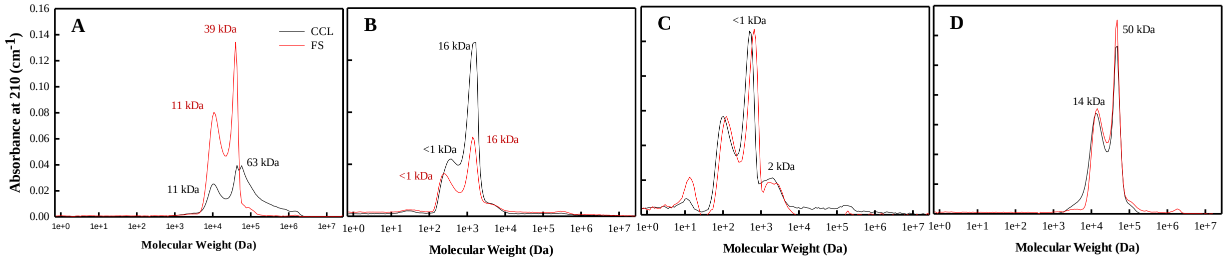

Figure 2: *The molecular weight cut-off at UV 210 nm for CCL and FS source water at (A) March (B) June (C) Sep. (D) Nov. in 2015*

3.2 Variations of Major Fluorescent Components of Source Waters after Alum Coagulation

Figure 3 shows the variations of major fluorescent components and residual turbidity of CCL source water by alum coagulation in different seasons. Based on March in 2015, as shown in Fig.3A, the residual turbidity ascended at the dosage of 0.5 mg Al^{3+}/L; however, the major

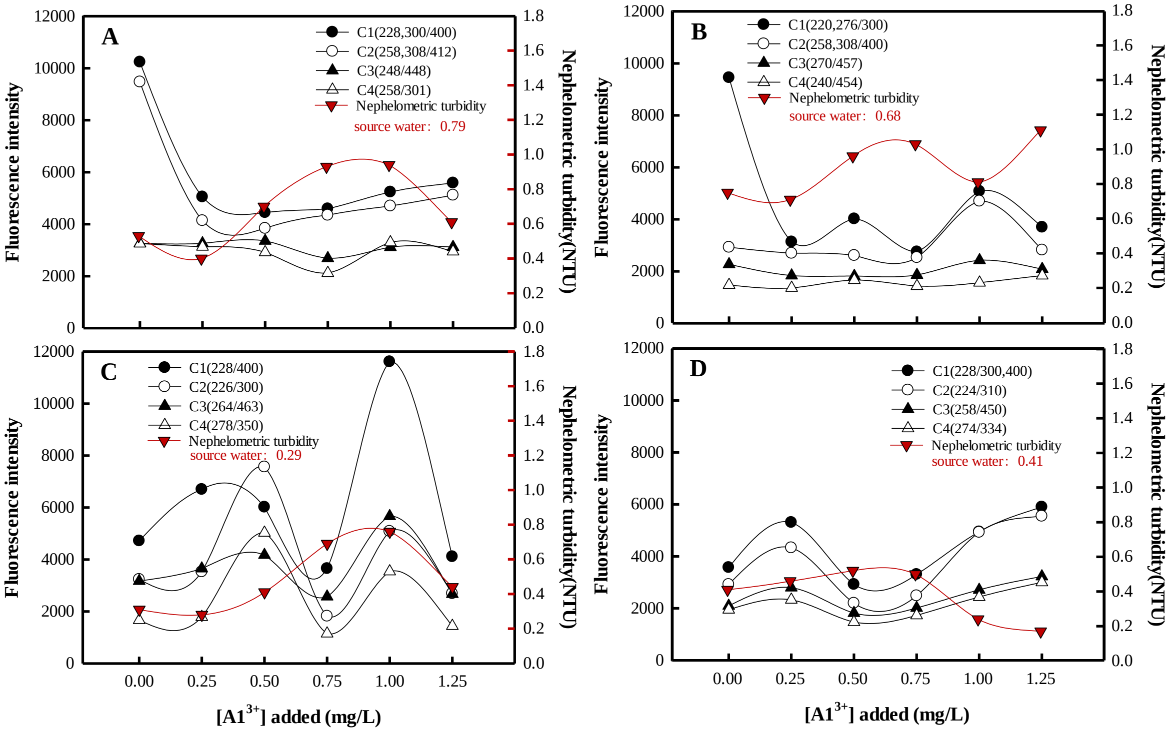

Figure 3: *The removal of main fluorescent components and turbidity by Jar Test for source water in CCL by Alum on (A)March (B) June (C) Sep. (D) Nov. in 2015*

components of 228,300/400 nm and 258,308/410nm could be effectively removed. The removal of major components of 248/448 nm and 258/310 nm was less than the other major fluorescent component at the dosage of 0.5 mg Al^{3+}/L. Optimal alum dosage for major components of 248/448 nm and 258/310 nm was higher than that of 228,300/400 nm and 258,308/410nm. For the residual turbidity on June in 2015, as shown in Fig.3B, the turning point was happened in 0.5 mg Al^{3+}/L; however, the removal of major components of 220,276/300 nm in 0.25 mg Al3+/L was higher than the other major components. The removal of major components of 248/448 nm and 258/310 nm was less than the other major fluorescent component at the dosage of 0.5 mg Al^{3+}/L. Optimal alum dosage for major components of 248/448 nm and 258/310 nm was higher than that of 228,300/400 nm and 258,308/410nm. For the optimal alum dosage for removing four components, same dosage was happened in 0.75 mg Al^{3+}/L. Signal intensity in 1.0 mg Al^{3+}/L was higher than that in 0.75 mg Al^{3+}/L. Finally, on Dec. in 2015, the major components of

228/300,400 nm and 224/310 nm could be effectively removed at the dosage of 0.5 mg Al^{3+}/L than the other major components. Residual turbidity could be more continuously removed until at the dosage of 1.25 mg Al^{3+}/L. Totally, most of major components could be effectively removed at the dosage of 0.75 mg Al^{3+}/L for CCL source water.

The variations of major fluorescent components and residual turbidity of FS source water by alum coagulation in different seasons are shown in Figure 4. The residual turbidity for four water samples at alum dosages added seemed like different. For the initial turbidity higher than 15 NTU, as shown in Fig.4 C, four fluorescent components could not be effectively removed by alum dosages added; however, residual turbidity was slow down less than 4 NTU at the dosage of 1 mg Al^{3+}/L. For the similar initial turbidity (close to 12 NTU) on March and June in 2015, as shown in Fig.4 A and 4 B, more turbidity on June in 2015 was removed at the dosage of 0.75 mg Al^{3+}/L than on March 2015. Meanwhile, only two major fluorescent components, like 220,276/300 nm and 258,308/400 nm, on June 2015 was apparently removed by alum of 0.75 mg Al^{3+}/L while only two major fluorescent components, 260/450 nm and 246/480 nm, on March 2015 were apparently removed by alum of 0.5 mg Al^{3+}/L. For the lowest initial turbidity (close to 12 NTU) on Dec. in 2015, as shown in Fig.4 D, turbidity could be not removed while alum dosage was controlled at 0.5 mg Al^{3+}/L; however, four major fluorescent components were slightly decreased.

3.3 Variation of Molecular Weight Cut-offs of Source Waters after Alum Coagulation.

For the variations of integrated area of different MWCOs after alum addition, most of water samples with less than 1 k Da could be not effectively removed and become larger even at high alum dosage except for the sample of FS on Sep. in 2015. Regarding to water samples with 10 k Da, integrated area of MWCOs was decreased with increasing alum dosage; however, dissimilar trend was happened in FS sample on March in 2015. Higher than 43 k Da of organic matter could be removed at 0.2 mg Al^{3+}/L , but ascending integrated area of MWCO was found while Alum dosage was higher 0.5 mg Al^{3+}/L. The phenomena of aggregation of low and high MWCOs were also observed while high alum dosage added.

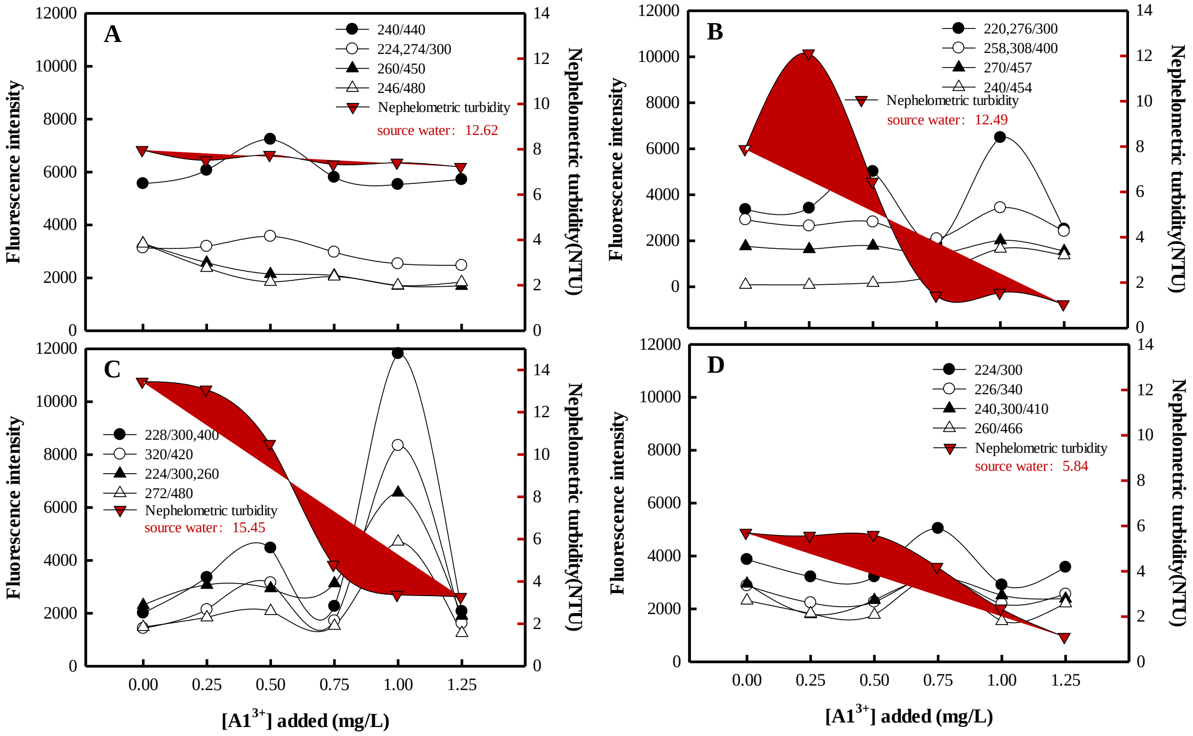

Figure 4: *The removal of main fluorescent components and turbidity by Jar Teast for source water in FS by Alum (A)March, (B) June (C) Sep. (D) Nov. in 2015*

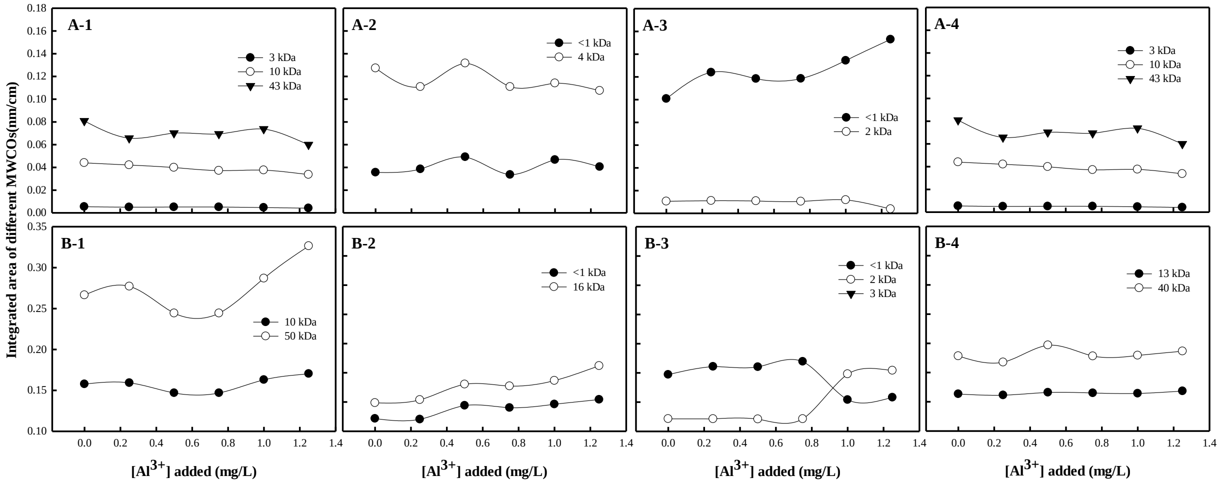

Figure 5: *The integrated area of different MWCOS at 210 nm (A) CCL (B)FS on (1)March (2) June (3) Sep. (4) Nov. in 2015*

4. Conclusions

In this study, several findings were summarized. Organic characteristics of source waters of FS and CCL were varied with the change of seasons, proving that four major fluorescent components appeared in whole samples. Regarding to MWCOs larger than 40 k Da, it was found on low flow seasons of March and Nov. The optimal alum dosage could be simultaneously affected by the initial turbidity as well as organic characteristic. Interestingly, 10 k Da of organic matter could be removed at adequate alum dosage added; however, the aggregation of lower or higher MWCO was found in high alum dosage added.

5. Acknowledgement

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