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Unveiling the transformation of dissolved organic matter in drinking water treatments based on FT-ICR-MS and spectral analysis

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Abstract The use of fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) and fluorescence excitation-emission matrix (EEM) systematically provide more comprehensive information on the changes in dissolved organic matter (DOM) composition and characteristic in water treatments. Therefore, this study aims to provide information on the molecular and spectroscopic characteristics of DOM in a full-scale drinking water treatment plant (DWTP) and summarize the effects of different treatment processes on DOM. This study sheds light on the molecular transformation of DOM in conventional treatments and advanced treatments.

Keywords: Drinking water treatments, Dissolved organic matter, FT-ICR MS, Spectral analysis

1. Introduction

The study identified the chemical composition of DOM from six sampling points. It revealed the high complexity and variability of DOM composition at the molecular level through spectroscopic and mass spectrometry analyses in a full-scale DWTP. In pursuit of high-quality drinking water, more drinking water treatment plants (DWTPs) begin to deploy pretreatment and advanced treatment process for removing refractory dissolved organic matter (DOM). Both the concentration and composition of DOM vary greatly in different sources and the variation is further complicated in DWTPs (Li et al., 2020). Besides, the reaction between chemical disinfectants (e.g., chlorine) and DOM results in the formation of disinfection byproducts (DBPs), which have adverse human health effects (Siddique et al., 2022). Characteristics of DOM play a vital role in the performance of removal treatments and are closely related to the water quality of treated water (Phong and Hur, 2016, Zhang et al., 2019). In recent years, a series of techniques have been used to characterize DOM in different water bodies and treatment processes. Fluorescence excitation-emission matrix (EEM) has been successfully used to track the quantity and quality of chromophoric and fluorescent DOM in water and characterize the efficacy of DOM removal in DWTPs (Moona et al., 2018). Meanwhile, Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) has helped unravel the molecular level changes of DOM in DWTPs with high precision (Cortés-Francisco et al., 2014, Li et al., 2019), which is probably the most powerful tool for studying the quality of DOM. The combination of fluorescence spectroscopy and FT-ICR MS could provide more comprehensive information on the complex DOM mixture and the behavior of DOM in water treatments. However, no study has systematically revealed the high complexity and variability of DOM composition at the molecular level through spectroscopic and mass spectrometry analyses in a full-scale DWTP. It is vital to identify the chemical composition of DOM so as to understand the fate of DOM and optimize the water treatment systems. Therefore, this study aims to provide information for the molecular and spectroscopic characteristics of DOM in a full-scale DWTP and summarize the effects of different treatment processes on DOM.

2. Materials and methods

The experiments were conducted at a full-scale DWTP (200,000 m3/d, Jintan, China) which uses Changdang Lake as its water source. It follows the water treatment processes: primary ozonation, coagulation and sedimentation, ozonation, BAC filtration (up-flow), sand filtration and chlorination. The performance of different processes was evaluated to understand DOM properties and efficacy of DOM removal from six sampling points: the raw water of Changdang Lake (RW), effluent of pre-ozonation (PRE), sedimentation (SED), ozonation (OZ), BAC filtration (BAC), and treated water (TW).

EEM measurement and FT-ICR MS were conducted on mixed water samples of triplicates collected on January 15th, 2020. Fluorescence spectroscopy (F-7000, Hitachi, Japan) was used to collect a three-dimensional EEM. The filtered samples were used to collect EEMs spectra using the same four-sided transparent quartz cuvette. Three-dimensional EEMs were collected with the following adjusted parameters; excitation (Ex) and emission (Em) wavelength ranges were both set at 200-600 nm with wavelength steps of 1 nm. Fluorescence regional integration (FRI) was used to integrate the volume beneath different EEMs regions (Maqbool et al., 2022). FT-ICR MS (Bruker SolariX, Germany) equipped with a 15.0 T superconducting magnet and an electrospray ionization (ESI) source operated in negative mode was used to analyze the DOM composition. The DOM components were categorized into seven compound classes based on the following criteria, (1) lipids (H:C $\geq$ 1.5; O:C = 0-0.3); (2) proteins (H:C $\geq$ 1.5; O:C = 0.3-0.67; N/C $\geq$ 0.05); (3) lignins (H:C = 0.7-1.5; O:C = 0.1-0.67); (4) carbohydrates (H:C $\geq$ 1.5; O:C = 0.67-1.2); (5) unsaturated hydrocarbons (H:C = 0.7-1.5; O:C = 0-0.1); (6) tannins (H:C = 0.7-1.5; O:C = 0.67-1.2); and (7) condensed aromatic structures (H:C = 0.2-0.7; O:C = 0-0.67) (Ohno et al., 2010). The mass-to-charge ratio range was set at 100-1000 m/z.

3. Results and discussion

3.1 Molecular characteristics of DOM

According to the molecular formulas of DOM detected by FT-ICR MS, we found that there were CHO, CHON, CHOS, CHOP, CHONP, CHONS, CHOSP, and CHONSP in all treatment process. Lipids (21.82%~44.33%) and lignins (24.11%~37.28%) compounds were predominant. Coagulation- sedimentation which was enhanced by pre-ozonation process had a good removal effect on CHONS, and chlorine disinfection process had the greatest impact on DOM. The molecular types of CHONSP and CHOP were increased by 183.59% and 141.91%, respectively.

3.2 Dynamic of fluorescent components in DOM

The fluorescence intensity decreased gradually during the drinking water treatments. It can be seen in TW that the integrated process has achieved more than 50% effective removal of five kinds of fluorescent components, among which the removal rate of humic acid-like substances was the highest (93.0%), which was obtained in Table S5 in Supporting Information. Conventional treatment had no significant effect on removing fluorescent DOM in raw water. However, after combine ozonation + BAC process, the fluorescence intensity was significantly reduced, indicating that the advanced treatment process had a better effect on the removal of fluorescent components. The removal rate of humic acid-like DOM was the highest (41.51%) and that of tyrosine-like was the lowest (7.38%) in the pretreatment-conventional process; the advanced treatment process also had the highest removal rate of humic-acid like substances (88.12%) and the lowest removal rate of dissolved microbial products (50.34%) compared with the SED samples.

3.3 Compositional changes in DOM

Lipids and lignins in DOM added up to 53.63%~81.56% in all water samples, and both kinds of DOM proportion declined eventually in TW, especially for lipids. Compared with RW, the types of DOM formulae in TW increased significantly, with an increase of 825.24%, 482.43% and 249.14% for carbohydrates, condensed aromatics and tannins, respectively. The types of proteins formulae also increased, while lipids, unsaturated hydrocarbons and lignins decreased.

The Fluorescence spectroscopy results showed the proportion of the tryptophan-like and SMPs-like DOM increased but tryptophan-like, fulvic-like and humic-like DOM decreased in the treatment processes. The RW sample was mainly composed of tryptophan-like substances.

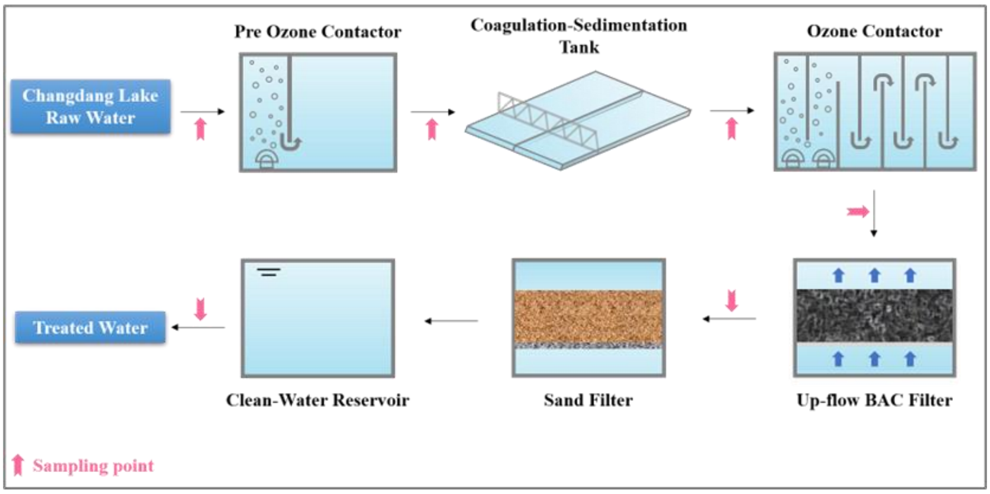

Figure 1. Schematic of a full-scale treatment process in the waterworks from Jintan, China.

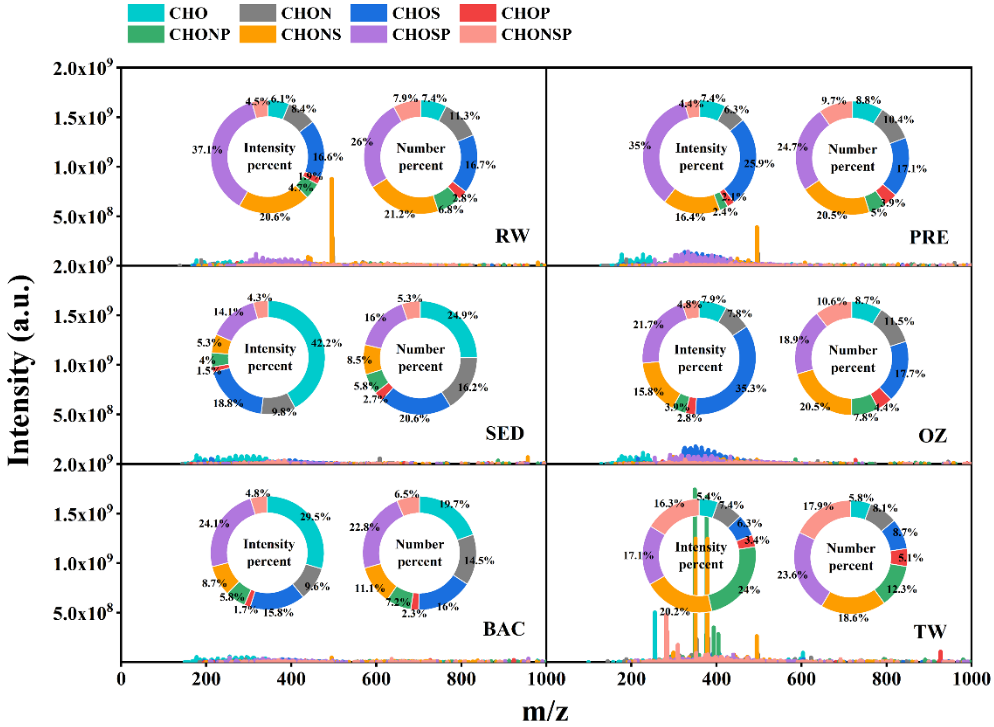

Figure 2. Relative intensities and number distributions of CHO, CHON, CHOS, CHOP, CHONP, CHONS, CHOSP, and CHONSP compound categories in water samples from the DWTP. The left and right charts are the proportions of response intensities and numbers in the different elemental compositions of the detected compounds.

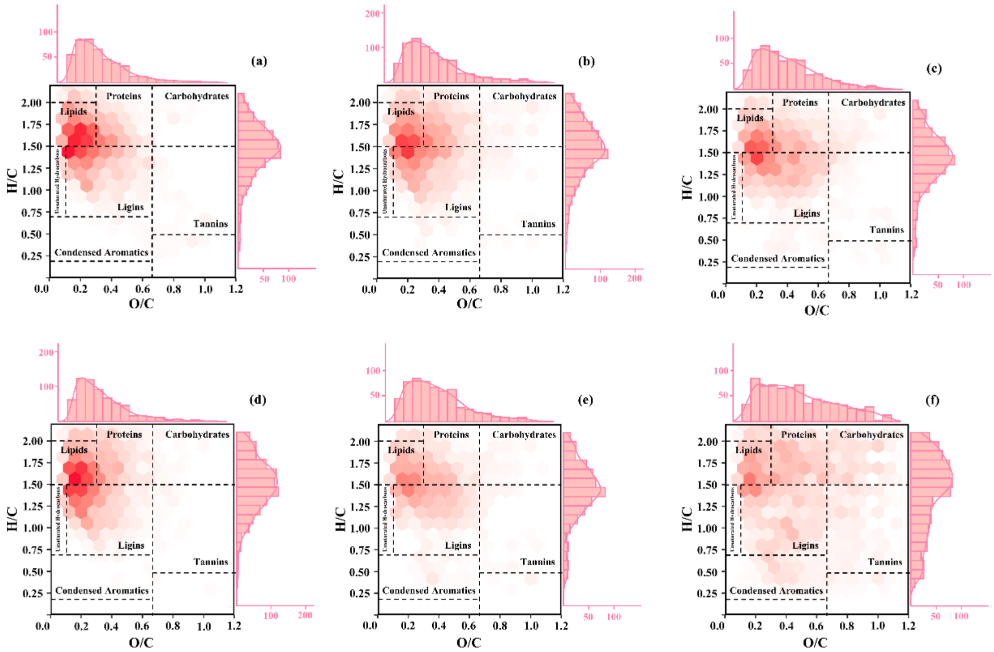

Figure 3. Van Krevelen density diagram of DOM in water samples from the DWTP. (a) RW; (b) PRE; (c) SED; (d) OZ; (e) BAC; (f) TW

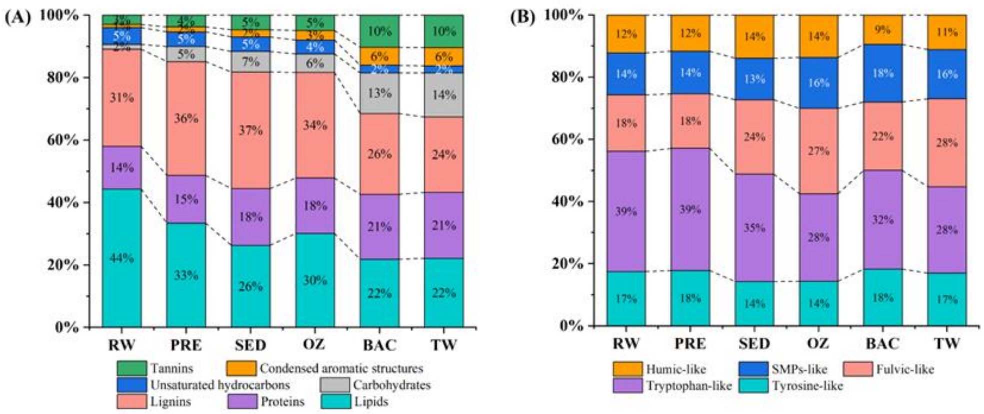

Figure 4. DOM composition in water samples from the waterworks using (A) FT-ICR MS; (B) EEM. Bar chart illustrates the proportion of major compound classes.

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