Application of UV and Fluorescence Indices for Assessing the Performance of Ozonation Process: Towards Smart Water Treatment

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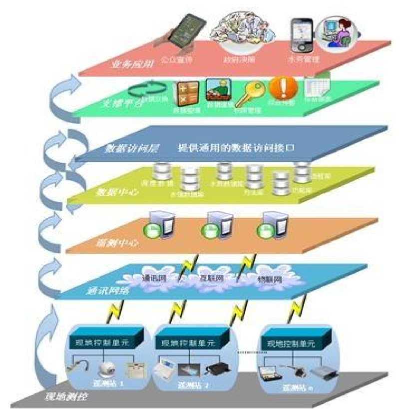
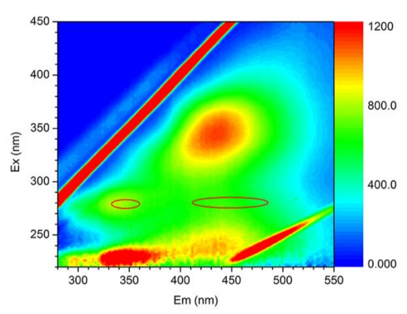
1. Background

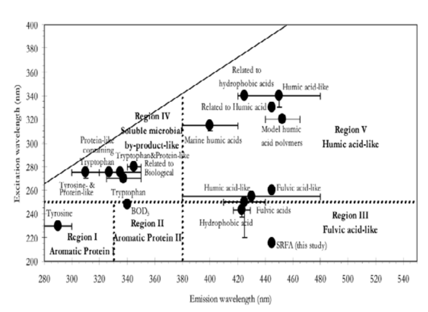


Smart Water treatment

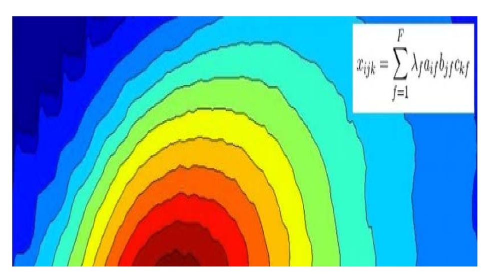
In the background of the Industrial 4.0, smart water treatment has drawn great interests. The smart water treatment system usually consists of four layers: sensor and actuator layer, communication layer, data processing layer and application layer. Dissolved organic matter, (DOM) including humic substances, proteins, and other aromatic or aliphatic organic compounds, plays important roles in water treatment processes, such as coagulation efficiency, membrane fouling, and disinfection byproducts. Therefore, the development of continuous online monitoring of DOM is urgent for the future smart cost-effective control during water treatment.



Excitation-Emission Matrix



Fluorescence Regional Integration [1]



Parallel Factor Analysis [2]

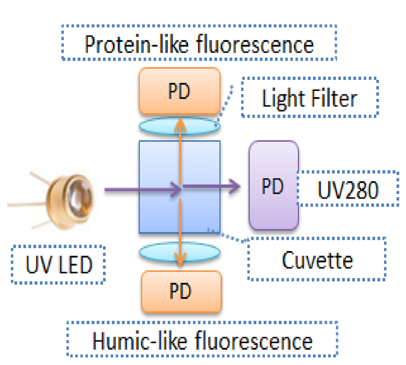
Excitation-Emission Matrix (EEM) as well as UV absorbance has been extensively applied for characterization of aquatic DOM. However, the two prominent data analyzing theories/methods including Fluorescence Regional Integration (FRI) [1] and PARAFAC analysis [2] are not behaving well for the interpretation of the fluorescent components in EEM.

By HPLC/HPSEC multi-excitation/emission fluorescence scan [3, 4, 5], we have confirmed that the fluorescence peaks at the same Em wavelength but different Ex wavelength are attributed to the same fluorophores, i.e., the definition of FRI was incorrect; the PARAFAC cannot reflect the real fluorescence characteristics of fluorophores. (For more information, see in our paper)

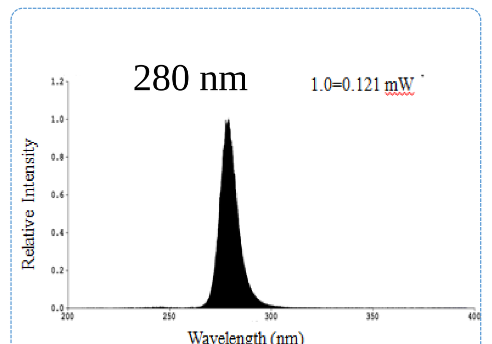
For frequent online monitoring, the fluorescence intensities of the marked area are sufficient to reflect the type and abundance of fluorophores that EEM can reflect, and we hereby developed a portable fluorimeter using an UV280 light emitting diode (LED) as light source and photodiodes as detectors [6].

2. Material and Methods

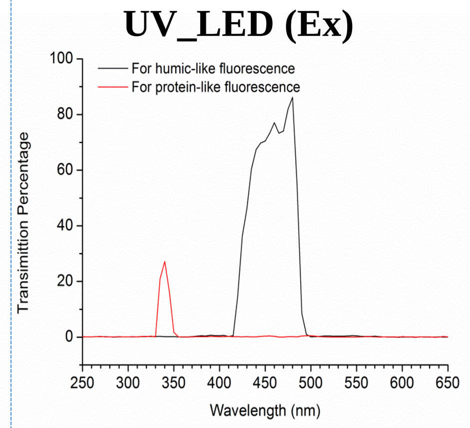
Lab Prototype



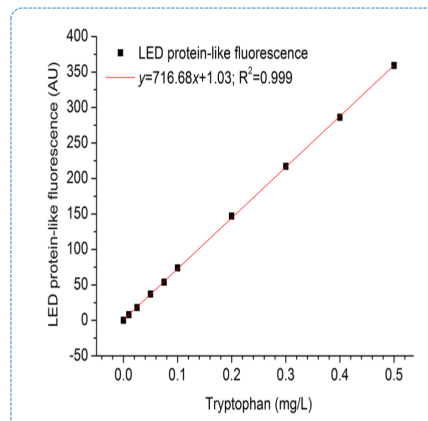
Inner Structure

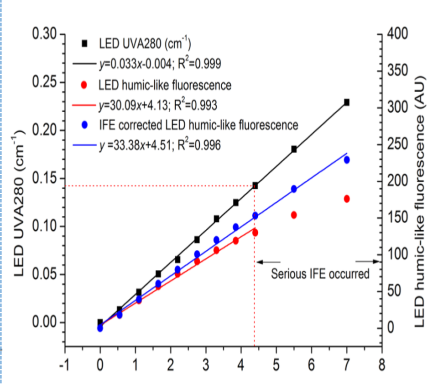


UV_LED (Ex)



Light Filter (Em)



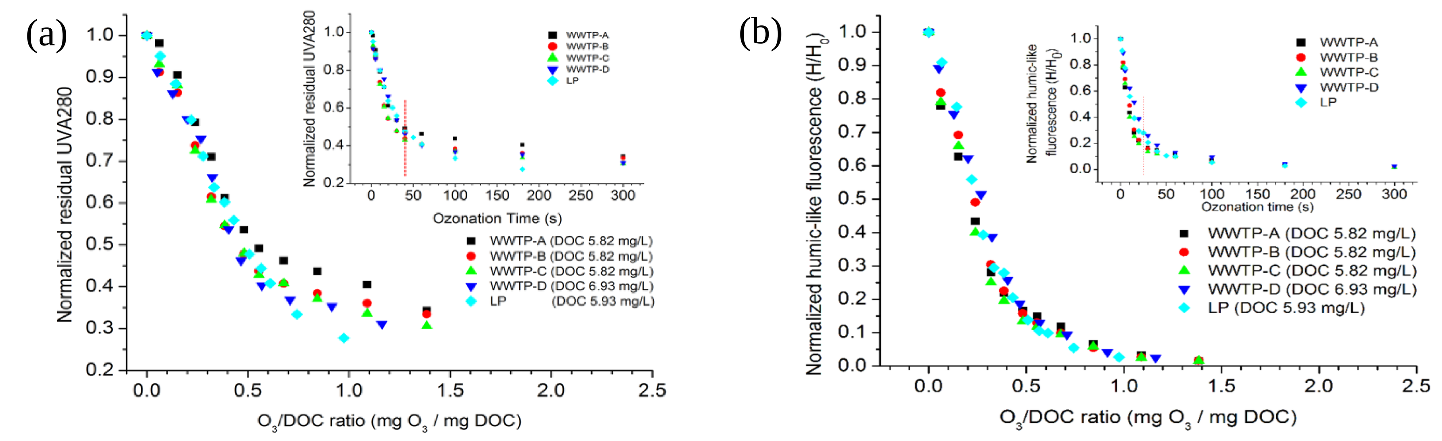


The newly developed LED UV/fluorescence sensor is capable of rapidly measuring UVA280 and protein-like and humic-like fluorescence. Especially, for the humic-like fluorescence, it has high a high sensitivity with a range of 30 ug/L – 10 mg/L as DOC, using the IHSS SR_NOM standard as reference.

For the other procedures and methods can be found in our published paper [7, 8].

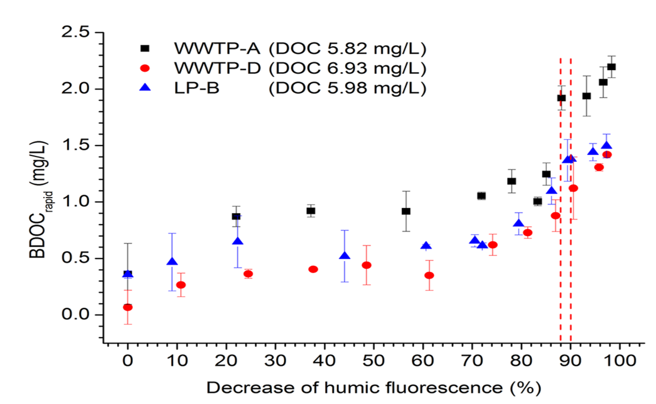
3. Results and Discussion

3.1 Degradation of Chromophores and Fluorophores [7]

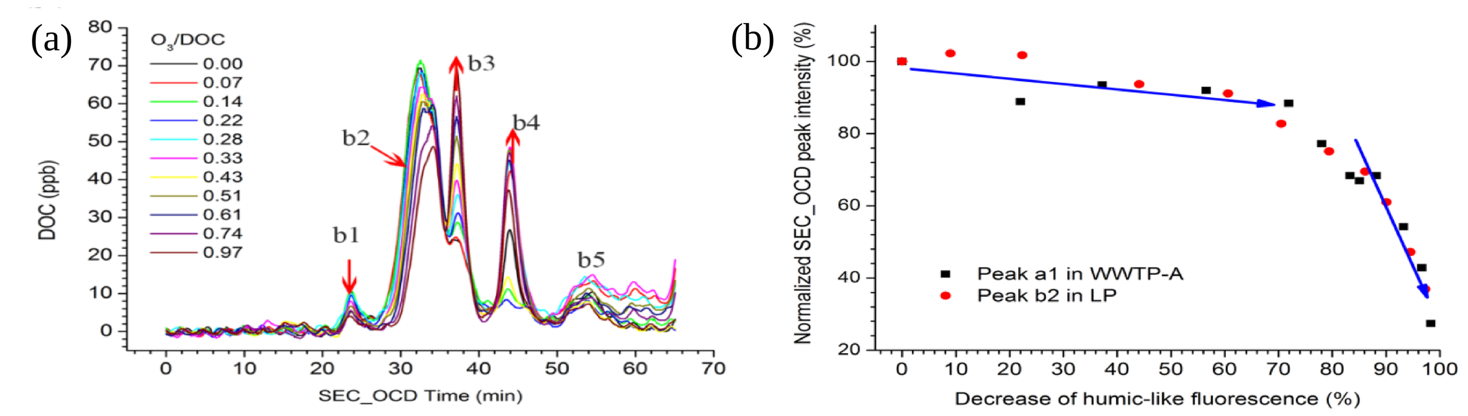


The plots of UV/fluorescence indices vs ozone dose or time showed two stages. For UV indices, the O_3/DOC ratios related to such inflection points were in the range of 0.4-0.6 mg O3/mg DOC. At these O3/DOC ratios, UVA254 and UVA280 were decreased by about 45-60%. For fluorescence indices, more than 80% of the humic-like fluorescence was lost in the initial stage e much higher than for the UVA indices. The O_3/DOC ratios related to such inflection points between these two stages were in the range of 0.3-0.4.

3.2 Molecular Weight Changes vs Ozone Doses & Fluorescence Reduction [7]

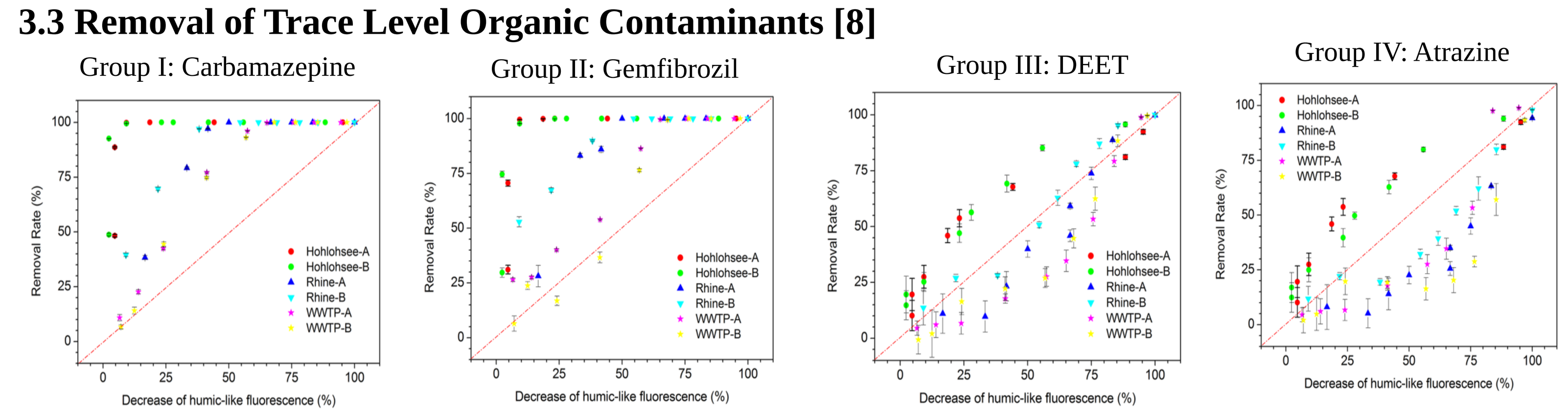


With the decrease of UV absorbance (not shown here) and fluorescence, biodegradable DOC concentrations initially increased slowly and then rose more noticeably. Inflection points in plots of BDOC versus changes of spectroscopic indicators were close to 35-45% loss of UVA254 or UVA280 and 75-85% loss of humic-like fluorescence.



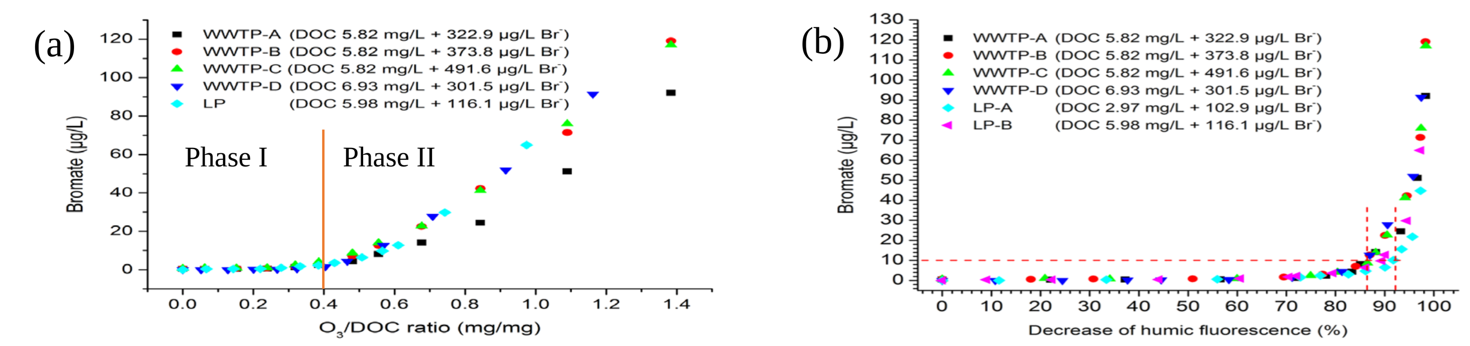
DOM fractions assigned to operationally defined large biopolymers (apparent molecular weight, AMW>20 kDa) and medium AMW humic substances (AMW 5.5-20 kDa) were transformed into medium-size building blocks (AMW 3-5.5 kDa) and other smaller AMW species (AMW<3 kDa) associated with BDOC at increasing O_3/DOC ratios.

3.3 Removal of Trace Level Organic Contaminants [8]



For TOrCs, their removal rates were well correlated with the decrease of the LED UV (not shown here) or fluorescence signals, and their elimination patterns were mainly determined by their reactivity with O3 and hydroxyl radicals. At approximately 50 % reduction of humic-like fluorescence almost complete oxidation of TOrCs of group I (e.g. carbamazepine) and II (e.g. gemfibrozil) was reached, a similar removal percentage (25-75 %) of TOrCs of group III (e.g. DEET) and IV (e.g. atrazine), and a poor removal percentage (< 25%) of group V (e.g. TCPP, not shown here). In another way, 90% reduction of humic-like fluorescence could reach the sufficient elimination of most TOrCs.

3.4 Formation of Bromate as a Function of O_3 Dose & Fluorescence Decrease [7]



Due to the initial O_3 demand during ozonation of high DOC water, the bromate formation was divided into two phase. Appreciable bromate formation was observed only after the values of UVA254, UVA280 and humic-like fluorescence in O_3-treated samples were decreased by 45-55%, 50-60% and 86-92% relative to their respective initial levels. No significant differences in plots of bromate concentrations versus decreases of humic-like fluorescence were observed for surface water and wastewater effluent samples, which facilitates the online prediction of bromate formation. An empirical equation applicable to the ranges of 6-7 mg/L DOC and 100-500 mg/L Br⁻ was obtained, as presented below:

$$BrO_3^- \ (\mu g/L) = 7.64 * 10^{-9} * e^{0.237 * HS(\%)}, \ R^2 = 0.962$$

4. Summary and Future Work

- These results suggest that measurements of humic-like fluorescence can provide a useful supplement to UVA indices for online evaluation and optimization of ozonation processes. Considering both water quality and treatment efficiency, ~90% decrease of humic-like fluorescence is recommended for ozonation.
- Currently, we are doing works to correlate the disinfection efficacy of pathogens with UV & fluorescence indices, and primary results showed that ~75% decrease of humic-like fluorescence reached to > 4 log inactivation of *E.coli*.
- Towards the smart water treatment, we are authorizing two companies: Shenzhen Kaitianyuan Automatic Engineering Co. (Shenzhen Water Group) and Shenzhen Bit_Atom Co. to develop the UV/fluorescence monitoring instruments.

5. Acknowledgements

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6. References & Publications

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[6] Li, W.-T. et al. Water Research 2016, 93, 1-9.
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