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

Wen-Tao Li (1), Gudrun Abbt-Braun (2), Michael Dodd (3), Gregory Korshin (3), and Ai-Min Li (1)

(1) Nanjing University, State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing, China (liwentaoepa@hotmail.com), (2) Water Chemistry and Water Technology, Karlsruhe Institute of Technology, Engler-Bunte-Ring 1, Karlsruhe 76131, Germany, (3) Department of Civil & Environmental Engineering, University of Washington, Box 352700, Seattle, WA 98195-2700, United States

The UV absorbance and fluorescence indices were comprehensively studied as surrogate indicators for assessing the degradation of dissolved organic matter (DOM), the formation of bromate and biodegradable dissolved organic carbon (BDOC) and the elimination of trace organic contaminants (TOrCs) during the ozonation of surface water and wastewater effluent. Spectroscopic monitoring was carried out using benchtop UV/Vis and fluorescence spectrophotometers and a newly developed miniature LED UV/fluorescence sensor capable of rapidly measuring UVA280 and protein-like and humic-like fluorescence.

With the increase of $O_3$/DOC mass ratio, the plots of BDOC formation were characterized three phases of initial lag, transition slope and final plateau. With the decrease of UV absorbance and fluorescence, BDOC 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. According to the data from size exclusion chromatography (SEC) with organic carbon detection and 2D synchronous correlation analyses, 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.

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. This was in contrast with the plots of bromate concentration versus UVA254 and UVA280 which exhibited sensitivity to varying initial bromide concentrations in the investigated water matrixes.

For TOrCs, their removal rates were well correlated with the decrease of the LED UV/fluorescence signals, and their elimination patterns were mainly determined by their reactivity with $O_3$ 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). In another way, 90% reduction of humic-like fluorescence could reach the sufficient elimination of most TOrCs.

These results suggest that measurements of humic-like fluorescence can provide a useful supplement to UVA indices for characterization of ozonation processes.