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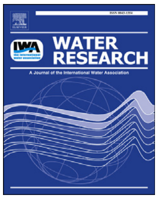

Application of UV absorbance and fluorescence indicators to assess the formation of biodegradable dissolved organic carbon and bromate during ozonation

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ABSTRACT

This study examined the significance of changes of UV absorbance and fluorescence of dissolved organic matter (DOM) as surrogate indicators for assessing the formation of bromate and biodegradable dissolved organic carbon (BDOC) 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 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. These results suggest that measurements of humic-like fluorescence can provide a useful supplement to UVA indices for characterization of ozonation processes.

1. Introduction

Ozonation has been widely used in drinking water and wastewater treatment for disinfection and oxidation purposes (Reungoat et al., 2012; von Gunten, 2003a, b; Zimmermann et al., 2011). Extensive studies have shown that ozonation results in significant elimination of adverse biological effects of many organic micropollutants (e.g., endocrine disrupting chemicals, antibiotics, and pharmaceuticals) as well as removal of color, odor and taste (Dodd et al., 2009; Hollender et al., 2009; Huber et al., 2005; Lee et al., 2012; Liu et al., 2012a; Nakada et al., 2007; Peter and von Gunten, 2007).

Ozone exposures required for disinfection and oxidation may result in the formation of undesirable organic and inorganic

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byproducts, including various disinfection byproducts (DBPs) and biodegradable dissolved organic carbon (BDOC) (von Gunten, 2003b; Wert et al., 2007). Ozonation has been shown to convert relatively refractory components of dissolved organic matter (DOM) into BDOC (e.g., aldehydes, carboxylic acids, ketones and etc.) without a significant decrease in overall dissolved organic carbon (DOC) concentration (Liu et al., 2015; Nishijima et al., 2003; Wert et al., 2007). The ozonation-derived BDOC in turn largely defines the biological stability of ozonated water, as it can contribute to increases in bacterial regrowth in drinking water distribution systems or wastewater effluent receiving waters (Escobar and Randall, 2001). As a result, ozonation is usually combined with a subsequent process of biological filtration to consume BDOC before the treated water is conveyed into a distribution system or a receiving water body. In this context, characterization of changes of molecular weights (MW) of DOM and evaluation of BDOC formation may provide a better understanding of integrated O_3 biofiltration processes for DOC removal.

In addition, ozonation of bromide-containing water or wastewater leads to the formation of bromate (von Gunten and Oliveras, 1998). Bromate is classified as a probable or likely human carcinogen, and many countries have established the maximum allowable level of bromate in drinking water at 10 μg/L (Butler et al., 2005). Unlike many organic DBPs, bromate is relatively stable and is difficult to remove using conventional treatment technologies (Butler et al., 2005; Nie et al., 2014). Although ecological impacts of bromate formation during wastewater ozonation are uncertain, the potential public health implications of bromate formation in potable water reuse scenarios utilizing ozonation could be significant. Hence it is of substantial interest to develop tools for better predicting and controlling bromate concentrations formed during both drinking water and wastewater ozonation.

The formation of BDOC and bromate, as well as the elimination of micropollutants, are directly related to the ozone exposure ($\int_0^t [O_3]dt$); that is, the time-dependent ozone concentration integrated over exposure time. An optimization of the ozone exposure is necessary to maximize the effect of oxidation and minimize the formation of undesired DBPs, especially BrO_3^-. However, for wastewater effluents, it is difficult to measure a dissolved O_3 residual during the initial O_3 demand stage (Gerrity et al., 2012; Wert et al., 2009). Additionally, direct analyses of BDOC and bromate are time-consuming and expensive. Therefore, the development of surrogate parameters for frequent online monitoring to enable more automated controls of ozone dosage is warranted. For example, the California Department of Public Health recently published a revised set of draft regulations for groundwater replenishment, which requires full advanced treatment facilities to identify at least one surrogate parameter that can be monitored continuously (Chon et al., 2015; Gerrity et al., 2012).

A number of studies have examined the performance of spectroscopic indicators, such as color, differential UV absorbance (UVA) and/or total fluorescence, and shown that such indicators were correlated with the removal efficiencies of organic micropollutants during ozonation (Gerrity et al., 2012; Li et al., 2016b; Liu et al., 2012b; Nanaboina and Korshin, 2010; Wert et al., 2009). Recently, Chon et al. (2015) applied the concept of electron donating capacity of DOM combined with UVA254 measurements to evaluate the degradation of micropollutants and the formation of bromate. Other studies have assessed the use of UVA254 and related indices to quantify the formation of individual ozonation byproducts associated with BDOC (Liu et al., 2012a).

Measurements of UV absorbance at 280 nm by means of UV light emitting diodes (LEDs) provide an attractive, energy-efficient alternative to conventional UVA254 monitoring (Bridgeman et al., 2015; Tedetti et al., 2013). UVA280 has previously been found to correlate well with DOM molecular weight and aromaticity and exhibit lower spectral overlap than UVA254 with inorganic species such as NO_3^- and NO_2^- that may interfere with measurements in many waters (Chin et al., 1994). In addition, measurements of DOM fluorescence at selected excitation and emission wavelengths provide a useful complement to UVA280 since fluorescence detection can also be implemented using LEDs and can enable more selective monitoring of chemically reactive protein-like and humic-like DOM components (Fimmen et al., 2007; Henderson et al., 2009). We recently demonstrated the use of a miniaturized LED UV/fluorescence sensor – capable of online measurement of UVA280, as well as protein-like and humic-like fluorescence – to predict DBP formation during chlorination (Li et al., 2016a).

The present study employs a sensor of this type to determine whether UVA280 and fluorescence indices may be used to develop correlations with BDOC and bromate formed during the ozonation of surface water and wastewater. To this end, degradation of DOM chromophores and fluorophores, MW changes, and formation of BDOC and bromate were examined during ozonation of a set of surface water and wastewater matrixes with varying initial bromide concentrations.

2. Material and methods

2.1. Water matrixes and reagents

Three water matrixes were used in the experiments described below. Secondary municipal wastewater effluent samples were taken from the West Point Treatment Plant in King County, WA (WWTP-I on Dec 14th, 2015 and WWTP-II on Feb 28th, 2016). This plant uses high-rate oxygen activated sludge technology without denitrification. The surface water was sampled from Lake Pleasant, which is a brown water eutrophic lake in Bothell, WA. Basic water characteristics of these waters are shown in Table 1. All the water samples were immediately filtered through a 0.45 μm membrane upon collection and stored at 4 °C before use.

The following chemicals were used in this study: sodium bromide (Sigma-Aldrich, >99%), sodium bromate (Sigma-Aldrich, >99%), polyethylene glycol standards (Alfa Aesar), methylamine solution (Sigma-Aldrich, 40 wt % in H_2O), and potassium indigotrisulfonate (Sigma-Aldrich).

2.2. Ozonation batch experiments

Five semi-batch ozonation experiments were performed at room temperature (25 ± 2 °C) with the three water matrixes mentioned above to explore the formation of BDOC and bromate

Table 1
Basic characteristics of water matrixes.

Parameters	WWTP-I	WWTP-II	Lake Pleasant
pH	6.92	6.95	7.48[a]
DOC (mg/L)	5.82	6.93	14.87
UV254 (cm^{-1})	0.130	0.139	0.727
UV280 (cm^{-1})	0.100	0.108	0.545
Conductivity (μs/cm)	480	652	314
Br^- (μg/L)[b]	267.8	201.5	36.7

[a] The pH values of 2.5 times diluted lake Pleasant water were about 7.

[b] The values listed here are the native background Br^- concentrations for each water matrix. Initial Br^- concentrations during ozonation batch experiments, using samples of each water matrix fortified with additional bromide, were as follows: 322.9 μg/L for WWTP-A, 373.8 μg/L for WWTP-B, 491.6 μg/L for WWTP-C, 301.5 μg/L for WWTP-D, and 116.1 μg/L for LP.