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# Effect of different molecular weight organic components on the increase of microbial growth potential of secondary effluent by ozonation

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## ABSTRACT

Ozonation has been widely applied in advanced wastewater treatment. In this study, the effect of ozonation on assimilable organic carbon (AOC) levels in secondary effluents was investigated, and AOC variation of different molecular weight (MW) organic components was analyzed. Although the removal efficiencies were 47%–76% and 94%–100% for UV<sub>254</sub> and color at ozone dosage of 10 mg/L, dissolved organic carbon (DOC) in secondary effluents was hardly removed by ozonation. The AOC levels increased by 70%–780% at an ozone dosage range of 1–10 mg/L. AOC increased significantly in the instantaneous ozone demand phase, and the increase in AOC was correlated to the decrease in UV<sub>254</sub> during ozonation. The results of MW distribution showed that, ozonation led to the transformation of larger molecules into smaller ones, but the increase in low MW (<1 kDa) fraction did not contribute much to AOC production. The change of high MW (>100 kDa and 10–100 kDa) fractions itself during ozonation was the main reason for the increase of AOC levels. Furthermore, the oxidation of organic matters with high MWs (>100 kDa and 10–100 kDa) resulted in more AOC production than those with low MWs (1–10 kDa and <1 kDa). The results indicated that removing large molecules in secondary effluents could limit the increase of AOC during ozonation.

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## Introduction

Water crisis is becoming increasingly serious all over the world, especially in some mega-cities and arid areas. The shortage of water resources limits social and economic development. Wastewater reclamation and reuse has become an attractive option for extending available water resources. Taking Beijing for example, the amount of reclaimed water used in 2012 was about 750 million m<sup>3</sup>, accounting for about 20% of the total water consumption.

Ozonation is widely applied in drinking water treatment and becomes increasingly common for advanced wastewater treatment for producing reclaimed water. Ozonation has been demonstrated to be very effective for color and odor removal, trace organic contaminant oxidation (Huber et al., 2005; Hollender et al., 2009; Wert et al., 2009), biotoxicity reduction (Huber et al., 2004; Escher et al., 2009; Misik et al., 2011), and microbial inactivation (Burns et al., 2007; Gerrity et al., 2011). Based on all these advantages, ozonation has been a promising technique for producing reclaimed water.

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However, the main problem for ozonation is that the biological stability of ozone oxidation treatment effluents generally becomes worse. The organic matter, especially the fraction called biodegradable organic matter, is generally the limiting nutrient for microbial growth in reclaimed water (Funamizu et al., 1998). Since ozonation does not mineralize the organic compounds completely, but only modifies the organic molecules in reclaimed water (Assalin et al., 2004; Medeiros et al., 2008; Audenaert et al., 2013). After ozone oxidation, the organic matter in water could be more biodegradable and more easily utilizable by microorganisms. The increases in assimilable organic carbon (AOC), which is often used as a significant indicator for the growth potential of heterotrophic microorganisms in water, have been observed after ozonation in both drinking water and reclaimed water treatment processes (Lehtola et al., 2001; Polanska et al., 2005; Hammes et al., 2006; Lai et al., 2006; Zimmermann et al., 2011; Thayanukul et al., 2013).

In drinking water, the mechanism for the increase of AOC during ozonation has been studied. Some researchers demonstrated that the oxidative breakdown of complex dissolved organic matters in water lead to the formation of low molecular weight (MW) organic compounds such as aldehydes, ketones and organic acids (Hammes et al., 2006; Wang et al., 2011). The formation of small molecules, which are more readily consumed by microorganisms, is the reason for AOC production by ozonation in drinking water.

The organic composition and concentration are different between drinking water and reclaimed water. Natural organic matter (NOM) accounts for the majority of organic component in drinking water, while the secondary effluent of the biological wastewater treatment process is a complex mixture of NOM, soluble microbial products originating from the activated sludge and recalcitrant organics (Barker and Stuckey, 1999; Shon et al., 2006). Therefore, the mechanism for AOC increase by ozonation in reclaimed water may be different from that in drinking water. So far, the previous studies only investigated the changes of AOC levels in reclaimed water during full-scale ozonation treatment (Zimmermann et al., 2011; Thayanukul et al., 2013). The reasons for AOC increase in reclaimed water have been rarely studied.

The objective of this study is to acquire the information on the impact of ozonation on AOC levels of municipal secondary effluents, and to analyze the reason for the changes by measuring the fractions with different MWs before and after ozonation.

## 1. Materials and methods

### 1.1. Sample collection and preparation

Water samples were collected from the effluent of secondary sedimentation tank of a municipal wastewater treatment plant (WWTP) in Beijing, China. Following primary sedimentation, the secondary biological treatment process of the WWTP is an anaerobic–anoxic–oxic process. The samples were collected from March 2013 to November 2013. Each sample of 20 L was collected into the organic carbon-free glass bottles, transported to the laboratory within 2 hr. All the samples were filtered by a 0.2 μm nylon membrane (Whatman, England, UK) to eliminate suspended solids, and stored at 4°C. The water quality was analyzed on the day of collection. The characteristics of the water samples are summarized in Table 1. Detailed information on the samples was listed in Appendix A Table S1.

### 1.2. Bench-scale ozonation test

In bench-scale ozonation test, the ozone stock solution was prepared first. Milli-Q water was placed into a glass flask and cooled to 0°C in an ice bath. Once cooled, 200 mg/L of gaseous ozone produced by an ozone generator (Newland, Fuzhou, China) was diffused into the water. The ozone generator was fed by ultra pure oxygen. After 2–3 hr, the ozone stock solution concentration could reach 50–60 mg/L. Dissolved ozone concentration in water was determined using the indigo trisulfonate colorimetric method according to Standard Methods 4500 (APHA et al., 2005).

The bench-scale ozone oxidation experiments were conducted in 1-L amber glass containers containing the respective secondary effluent samples at room temperature (20°C). Defined volumes of ozone stock solution were injected into the container to achieve an ozone dosage range of 1–10 mg/L. After a reaction time of 30 min, each solution was added sufficient sodium thiosulfate to quench any residual ozone. The maximum concentration of residual ozone after a 30 min reaction was less than 0.5 mg/L.

The instantaneous ozone demand (IOD) of the samples was determined according to the method of Xu et al. (2002). After the ozone stock solution was added into the sample, the residual ozone concentration was measured within 30 sec. IOD represents the minimum ozone dosage to get the measurable ozone residual in the sample.

### 1.3. Molecular weight fractioning

MW distribution of the organic matter in water sample was measured using regenerated cellulose ultrafiltration membranes with MW cut offs of 1, 10 and 100 kDa (Millipore, Billerica, MA, USA). Parallel processing of samples through different membranes was chosen due to its smaller error in determining MW distribution (Logan and Qing, 1990).

Before fractionation, the sample was filtered by a 0.2-μm microfiltration membrane to remove the particulate matters. Then, 350 mL of the sample was poured into the stirred ultrafiltration cell (Model 8400, Millipore, Billerica, MA, USA), and the cell was placed on the magnetic stirring table. Membrane filtration was driven by pure nitrogen at an operation pressure of 0.05–0.4 MPa according to the type of the membrane. Filtration was stopped when the volume of residual sample in the cell reduced to 50–100 mL. Finally, the filtrate with lower MW organic matters was collected for

**Table 1 – Characteristics of the secondary effluent samples investigated in this study.**

Parameters	Range of values	Average
pH	7.3–8.3	
DOC (mg/L)	4.7–13.9	8.5
UV <sub>254</sub> (m <sup>-1</sup> )	10.0–15.2	12.1
NH <sub>3</sub> -N (mg/L)	0.1–0.4	0.2
TN (mg/L)	6.4–27.8	17.1
TP (mg/L)	2.2–2.7	2.5
Color (C.U.)	13.5–17.0	15.0

DOC, dissolved organic carbon; UV<sub>254</sub>, the absorbance at 254 nm; NH<sub>3</sub>-N, ammonia nitrogen; TN, total nitrogen; TP, total phosphorus.

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