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A study on the reactivity characteristics of dissolved effluent organic matter (EfOM) from municipal wastewater treatment plant during ozonation

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ABSTRACT

The reactivity of dissolved effluent organic matter (EfOM) in the process of ozonation was examined. Under different ozone dosages (0.42 ± 0.09, 0.98 ± 0.11 and 2.24 ± 0.17 mgO_3/mg DOC), the EfOM before and after ozonation could be classified into four fractions according to their hydrophobicities. By ozonation, the hydrophobic fractions, especially hydrophobic acid (HOA) and hydrophobic neutral (HON), were found to undergo a process of transformation into hydrophilic fractions (HI), of which the HOA were first transformed into HON, and then the majority of the HON fraction was later converted to HI by further ozonation. It was noticeable that after ozonation, the fluorescence intensity in the humic-like and protein-like regions decreased as indicated by the excitation and emission matrix (EEM) spectra for the hydrophobic fractions. By coupling the EEM spectra with the molecular size analysis using high performance size exclusion chromatography (HPSEC), the difference between the characteristic distributions of the humic-like and protein-like fluorophores were further revealed. It could thus be extrapolated that ozone might have preferentially reacted with the protein-like hydrophobic fraction with molecular weight (MW) less than 100 kDa. Moreover, by X-ray photoelectron spectroscopy (XPS) analysis, it was identified that with increasing ozone dosage (from 0 to 2.24 ± 0.17 mgO_3/mg DOC), the aromaticity of HON decreased dramatically, while aliphatics and ketones increased especially at the low ozone dose (0.42 ± 0.09 mgO_3/mg DOC). Of the EfOM fractions, the HON fraction would have a higher content of electron enriched aromatics which could preferentially react with ozone rather than the HOA fraction.

1. Introduction

Dissolved effluent organic matter (EfOM) after conventional biological treatment is a mixture of soluble microbial products (SMP) (Barker and Stuckey, 1999), natural organic matter (NOM) conveyed from drinking water sources (Filloux et al., 2012) and xenobiotic micropollutants (Audenaert et al., 2013). In cases where the effluent is disinfected by chlorine, EfOM can also contain chlorinated disinfection byproducts (Krasner et al., 2009). The majority of residual organic compounds present in EfOM are slowly biodegradable or recalcitrant.

Reclaimed water has become a very important water source in water deficient areas and one of the top issues concerning the water reuse is the safety of reclaimed water. However, conventional water reclamation process (coagulation-sedimentation-filtration) is not considered sufficient to secure the reuse safety. In this case, oxidation processes are often applied to minimize the risk of negative environmental and health effects due to exposure to micropollutants and disinfection byproducts (Galapate et al., 2001; Jin et al., 2013). Among the different oxidation processes, ozone is often applied because of its high oxidation potential (Sadrnourmohamadi and Gorczyca, 2015; Rodríguez et al., 2012; Owen et al., 1995; Reckhow and Singer, 1984) and compared to

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advanced oxidation processes (like e.g. UV/H_2O_2), ozonation is an energy efficient solution for transformation of most recalcitrant organic micropollutants (Sonntag and Von Gunten, 2012). Therefore, knowledge about changes in the chemical properties of EfOM during ozonation is important because it is closely related to their reaction pathways, the trihalomethanes formation potential (THMFP), and downstream treatment process efficiency.

Ozonation directly influences both the composition and chemical properties of EfOM. Especially important chemical features such as hydrophobicity/hydrophilicity and acid/base behaviours, which are important for EfOM distribution in the water phase and its interactions with other dissolved compounds and colloids/particles (Gong et al., 2008), are altered. Therefore, knowledge about changes in these chemical properties of EfOM during ozonation are important, when wastewater effluents are discharged to the environment or being reused (Chiang et al., 2002). Fractionation through XAD macroporous resins, which are commonly used for the fractionation of dissolved organic matter (Matilainen et al., 2011), is a favourable way to obtain information about changes in the hydrophobicity/hydrophilicity and acid/base behaviours of EfOM during ozonation. Fractionation by XAD resin has been frequently applied to study the reactivity between NOM and oxidants, such as ozone and chlorine dioxide (Galapate et al., 2001; Chiang et al., 2002; Marhaba et al., 2000; Świetlik et al., 2004; Yan et al., 2007; Zhang et al., 2008a; Bose and Reckhow, 2007). Nonetheless, the detailed transformation pathways remained poorly understood in these studies. As for the fractionation of EfOM in general, Imai et al. (2002) analysed the fraction distribution of EfOM from wastewater treatment plants (WWTPs), while Zhang et al. (2009) studied the THMFP and haloacetic acids formation potential (HAAFP) of isolated EfOM fractions. However, there is relatively little data available. Furthermore, there are few studies describing the effects of ozonation on EfOM (Gong et al., 2008).

Fluorescence spectroscopy can provide important information about the chemical nature of the EfOM because the position, shift and intensity of fluorescence peaks can be correlated with molecular structural information (Chen et al., 2003). To characterize the fluorescent dissolved organic matter (DOM) in wastewater effluents, this technique has been extensively used (Quaranta et al., 2012; Wang et al., 2009). Further, high-performance size exclusion chromatography (HPSEC) can provide information about the molecular size of DOM (Sarathy and Mohseni, 2007; Bazri et al., 2012). The molecular size of fluorescent DOM can be determined when HPSEC is combined with fluorescence detection, by using selected pairs of excitation/emission (Ex/Em) wavelengths in the EEM spectra. This was previously done by Nagao et al. (2003), Bourven et al. (2012) and Bhatia et al. (2013). However, they focused on NOM and extracellular polymeric substance (EPS), instead of EfOM. HPSEC coupled with fluorescence detection is well-suited to resolve different fluorophores within different fractions in EfOM. Furthermore, the variation of functional groups of different fractions in EfOM is important reactivity characteristics during ozonation as well. However, there are very few works focussing on the functional groups transformation in different fractions during ozonation. Zheng et al. (2014) only obtained the isolated fractions from EfOM using ^{13}C nuclear magnetic resonance (NMR) without further information about molecular structure variation during ozonation. X-ray photoelectron spectroscopy (XPS) can be used to determine the functional groups in organic matters, and it has been extensively used in the analyses of functional groups in EPS in recent years (Yin et al., 2015; Hou et al., 2015; Badireddy et al., 2010).

Thus, the main objective of this study was to investigate the reactivity of dissolved EfOM during ozonation at different ozone dosages to provide useful information for evaluation of reaction pathways, which subsequently can be used for ozone dosage selection during water reclamation, improved risk control for reclaimed water, and possible downstream treatment process optimization. In order to obtain a better understanding of the fingerprints variation of humic-like and protein-like substances in different fractions during ozonation, HPSEC with fluorescence detection was applied. XPS was used to analyse the effect of ozonation on functional groups for the different fractions of EfOM to facilitate determining the detailed transformation pathways between different fractions.

2. Materials and methods

2.1. WWTP and water samples

The water used in this study was effluent wastewater with pH of 7.33 ± 0.23 collected before the disinfection step at the effluent of the sedimentation tank in a municipal wastewater treatment plant (WWTP) in Xi'an, China. The WWTP consists of a biological Anaerobic-Anoxic-Oxic treatment process that treats mainly domestic wastewater. The capacity of the WWTP is 500,000 m^3/d with hydraulic retention time (HRT) 20 h and sludge retention time (SRT) 19 d. The effluent of the WWTP typically has the following characteristics: 42.2 ± 4.6 mg/L COD, 12.8 ± 1.7 mg/L total nitrogen and 0.24 ± 0.13 mg/L total phosphorus. The water samples were filtered using a 0.45 μm filter (Shanghai Xinya, China) for the removal of particles prior to ozonation. The filtered raw water quality is shown in Table 1.

2.2. Experimental setup

The experimental ozonation setup is shown in Fig. 1. The effective volume of the reactor was 2.0 L. The ozonated water sample was collected to meet the demand of concentration and fractionation. The feed gas flow from the ozone generator (WH–S–B2, Nanjing Wohuan, China) was maintained at 40 L/h. Unreacted ozone in the off gas from the reactor was destructed in a 20% KI trap. The reactor temperature was kept constant at 15 °C by a water bath. Nitrogen gas was fed to the reactor for 5 min to strip the remaining ozone from the water in the reactor. The ozone dosage was determined according to Kasprzyk-Hordern et al. (2006) and Galapate et al. (2001). The reacted ozone dosage in this study was determined by the difference between pre-determined in–gas amount of ozone and off-gas ozone trapped by 20% KI solution. The reacted dosage of the ozone was adjusted by the reaction time. The ozonation experiments were performed in triplicate and the results are presented as the mean values with standard deviations. In this study, three different ozone dosages were applied respectively, 0.42 ± 0.09, 0.98 ± 0.11 and 2.24 ± 0.17 mgO_3/mg DOC.

2.3. Fractionation procedure

All of the filtered samples, raw water and ozonated samples, were concentrated by a reverse osmosis membrane system (Mosutech, China). The concentration degree was 20, namely each 1-L water sample was concentrated to 50 ml. The characteristics of the concentrated samples before and after ozonation are shown in Table 2. The fractionation was performed with the XAD resin method, which was modified from Imai et al. (2002), Leenheer (1981), Pernet-coudrier et al. (2008) and Zhang et al. (2009). XAD-8 resin from Supelco was used in this study. The resin was first purified by Soxhlet extraction with methanol before being used in fractionation. During the fractionation, 150 mL of a concentrated water sample (raw or ozonated) was pumped through the resin. The first adsorbent from XAD-8, hydrophobic base (HOB), was then