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Carbonaceous and nitrogenous disinfection byproduct precursor variation during the reversed anaerobic–anoxic–oxic process of a sewage treatment plant

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ABSTRACT

Disinfection byproduct (DBP) precursors in wastewater during the reversed anaerobic–anoxic–oxic (A^2/O) process, as well as their molecular weight (MW) and polarity-based fractions, were characterized with UV scanning, fluorescence excitation emission matrix, Fourier transform infrared and nuclear magnetic resonance spectroscopy. Their DBP formation potentials (DBPFPs) after chlorination were further tested. Results indicated that the reversed A^2/O process could not only effectively remove the dissolved organic carbon (DOC) and dissolved total nitrogen in the wastewater, but also affect the MW distribution and hydrophilic–hydrophobic properties of dissolved organic matter (DOM). The accumulation of low MW and hydrophobic (HPO) DOM was possibly due to the formation of soluble microbial product-like (SMP-like) matters in the reversed A^2/O treatment, especially in the anoxic and aerobic processes. Moreover, DOM in the wastewater displayed a high carbonaceous disinfection byproduct formation potential (C-DBPFP) in the fractions of MW > 100 kDa and MW < 5 kDa, and revealed an increasing tendency of nitrogenous disinfection byproduct formation potential (N-DBPFP) with decrease of MW. For polarity-based fractions, the HPO fraction of wastewater showed significantly higher C-DBPFP and N-DBPFP than hydrophilic and transphilic fractions. Therefore, although the reversed A^2/O process could remove most DBP precursors by DOC reduction, it led to the enhancement of DBPFP with the formation and accumulation of low MW and HPO DOM. In addition, strong correlations between C-DBPFPs and SUVA, and between N-DBPFPs and DON/DOC, were observed in the wastewater, which might be helpful for DBPFP prediction in wastewater and reclaimed water chlorination.

Introduction

Wastewater reclamation is considered an effective approach to improve the utilization efficiency of water resources and alleviate water shortages. In order to reduce the potential ecological and health risks of reclaimed water, disinfection has been utilized as the last barrier in wastewater reclamation to inactivate microorganisms, and is of great importance to the safety of reclaimed water. Chlorination is most widely applied because of its high disinfection efficiency, low cost

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and provision of sufficient residual chlorine (Cl_2). However, disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), are produced from the reaction between free Cl_2 and dissolved organic matter (DOM) (Yang and Zhang, 2013; Liu and Zhang, 2014), which have been proved to be carcinogenic, mutagenic, and teratogenic (Liu et al., 2014; Chang et al., 2011). Although reclaimed wastewaters are mainly used for agricultural irrigation and urban miscellaneous water (lawn watering, recreational amenities, road cleaning, car washing, toilet flushing, *etc.*), rather than as sources for drinking water (González et al., 2013), they are likely to influence human health by lung inhalation and skin absorption directly, and/or by migration to drinking water sources through surface water transfer and groundwater infiltration indirectly. Moreover, recent studies have found that the upper reaches of many water sources have been polluted by wastewaters and discharge of their treated effluents (Liu et al., 2014; Chen et al., 2009), which could greatly affect drinking water quality. Hence, it is of great importance to address the concerns raised by wastewater-derived DBPs.

DBP formation was reported to be affected by the dissolved organic carbon (DOC), dissolved organic nitrogen (DON), ammonia nitrogen (NH_4^+–N), bromide (Br^-) concentration and disinfection operating conditions (*e.g.*, free Cl_2 dosage, disinfection time, pH and temperature) (Ma et al., 2013a; Wu et al., 2010; Sun et al., 2009a, 2009b). Among these, DOM as the primary DBP precursor, contributed the most important components of DOC and DON in the reclaimed water. DOM in bio-treated municipal wastewater is more complex than that in drinking or source water, with various components that are significantly different. DBP precursors might be derived from the raw water, with constituents such as synthetic organic chemicals and natural organic matter (NOM, mainly humic acids and fulvic acids). Biological physico-chemical processes during wastewater treatment could also result in the production of DBP precursors such as soluble microbial products (SMPs, mainly protein, polysaccharide and nucleic acid) and other transformed products (Ma et al., 2015). For example, Sirivedhin and Gray (2005) discovered that the effluent of biological wastewater processes had a higher DBP formation potential (DBPFP) after chlorination, compared to drinking water. Substantial levels of DBPs were found during the chlorination of well-nitrified and poorly nitrified effluents, especially for nitrogenous DBPs (N-DBPs) and brominated DBPs (Br-DBPs). These wastewater organic and/or inorganic pollutants would increase DBP precursors in the effluents, resulting in more DBP formation in the reclaimed water (Chen et al., 2009; Krasner et al., 2009). Therefore, the characteristics of wastewater DOM and the formation of DBPs deserve further consideration.

Improved knowledge of DOM in reclaimed water is necessary for DBP precursor identification. Various quantification approaches such as measurement of DOC, DON and Specific UV absorbance (SUVA), as well as a number of characterization methods such as high performance size exclusion chromatography (HPSEC), fluorescence excitation emission matrix (EEM), Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR), have been applied to discriminate the bulk chemical properties of DBP precursors (Huang et al., 2016; Peleato and Andrews, 2015; Iriarte-Velasco et al., 2008; Zhao et al., 2009; Gonsior et al., 2014; Zheng et al., 2016). Furthermore, high resolution mass spectroscopy such as quadrupole time-of-flight mass spectrometry (Q-TOF-MS) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) have been used to perform non-targeted screening of unknown DBPs and their precursors (Sultan and Gabryelski, 2006; Wang et al., 2016). Before DBP precursor characterization, DOM is usually fractionated into more homogenous components in order to gain a better understanding of its characteristics. Yang et al. (2008) separated NOM into four fractions by XAD-8 and XAD-4 resins to identify NOM properties and DBP formation during chloramination. Chang and Wang (2013) fractionated DON constituents in treated wastewater effluents and raw water using XAD-8, XAD-4 and MSC-1H resins for better composition characterization and identification. Han et al. (2015) further used ultrafiltration (UF) membranes and XAD-8 resins to determine the removal of THM precursors by coagulation and adsorption for bio-treated municipal wastewater. Overall, polarity and molecular weight (MW) based separation of DOM has proved to be effective and reasonable for DBP precursor screening.

DBP precursor removal before disinfection appears to be an effective method for DBP control in reclaimed water and drinking water. Physico-chemical treatment such as coagulation and adsorption, membrane filtration, activated carbon filtration and advanced oxidation has been widely applied for DBP precursor control during reclaimed water and drinking water treatment. Little study has been carried out to investigate the function of biological processes in DBP precursor transformation. As biological processes contribute significantly to DBP precursor transformation, such as DOC removal, DON conversion, dissolved inorganic nitrogen (DIN) formation and SMP accumulation, screening and control of DBP precursors during wastewater reclamation deserve further consideration. Hence in this study, a widely applied biological process (reversed A^2/O) during municipal wastewater treatment in China was examined. The objectives were: (1) to identify and characterize DBP precursors in the process using polarity- and MW-based separation, (2) to evaluate DBP precursor transformation products and their formation potentials, (3) and to determine the relationship between the specific DBP precursors or parameters and DBP species during this process.

1. Materials and methods

1.1. Chemicals and reagents

DBP standards such as THM_4 (Supelco 47904), HAA_9 (Supelco 49107-U), haloketone$_2$ (HK_2, Supelco 48046), chloral hydrate (CH, Supelco 47335), haloacetonitrile$_4$ (HAN_4, Supelco 48046), and halogenated nitromethane (HNM, Supelco 48046) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). The extraction solvent 99.9% methyl *tert*-butyl ether (Chromasolv® Plus-grade MtBE) was acquired from Sigma-Aldrich. Other reagents used for sample fractionation, characterization and disinfection during the investigation were at least of analytical grade and mainly from Sigma-Aldrich. Ultrapure deionized water (18 MΩ·cm, DI water) was prepared in the lab using a Milli-Q water system (Millipore, USA).

The water samples used in this study were collected from the reversed A^2/O process of Taihu Xincheng wastewater