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Transformation of anti-estrogenic-activity related dissolved organic matter in secondary effluents during ozonation

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ABSTRACT

Anti-estrogenic activity of dissolved organic matter (DOM) in reclaimed water is gaining increasing attention. In this study, anti-estrogenic activity removal efficiency by ozonation in the tertiary treatment process of domestic wastewater was investigated. The anti-estrogenic activity in the secondary effluents used in this study ranged between 0.95 and 2.00 mg-TAM L^{-1} and decreased significantly after ozonation. The removal efficiency of anti-estrogenic activity at a dose of 10 mg-O_3 L^{-1} was 65–87%. The removal of the anti-estrogenic activity was highly correlated with the removal of UV_{254}, suggesting that UV_{254} can be used as a surrogate for anti-estrogenic activity during ozonation. The results of size exclusion chromatography of the wastewater samples during ozonation showed that the UV_{254} absorbance of the DOM fraction with large apparent molecular weight (MW) around 7.6 k Da dropped significantly, and the DOM fraction was suspected to be humic substances which have been previously identified as anti-estrogenic constituents in secondary effluents. The excitation emission matrix fluorescence spectra of the wastewater samples proved that humic substances existed in the DOM and indeed reacted with the ozone. With the help of two-dimensional correlation of Fourier transform infrared, it was confirmed that the aromatic structures in the DOM were largely destroyed by ozonation. Therefore, it was suggested that the destruction of the aromatic structures in the DOM was related to the removal of the anti-estrogenic activity.

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1. Introduction

Wastewater reclamation and reuse is a practical solution to water resource shortages which are becoming a worldwide problem (USEPA, 2004). However, in reclaimed water, there are complex organic constituents, which may be biotoxic or precursors of toxic by-products. As previously reported, toxic organic constituents discharged into rivers may lead to birth defects in the offspring of fish, which may increase the risk of ecological damage (Shon et al., 2006; Richardson et al., 2007; Steinberg et al., 2009).

In order to assess the safety of the reclaimed water, bioassays are increasingly employed to monitor the potential ecological impacts, such as endocrine disrupting effects as well as genotoxicity in the reclaimed water (Shiraishi et al., 2001; Wang et al., 2007; Watsona et al., 2012). In recent years, many researchers have attached great importance to the endocrine disrupting effects induced by dissolved organic matter (DOM) in drinking water and reclaimed water (Campbell et al., 2006; Vega-López et al., 2007; Wang et al., 2007; Watsona et al., 2012; Maggioni et al., 2013). Among all the effects, anti-estrogenic activity is attracting increasing attention, because anti-estrogenic chemicals were reported to antagonize the actions of steroid hormones, disrupt the estrous cycle and result in preimplantation loss of females in animal studies (Hodgson, 2004). However, the changes and removal of anti-estrogenic activity during water treatment was seldom known.

Organic chemicals with anti-estrogenic activity in surface water and wastewater, such as polynuclear aromatic hydrocarbons (Tran et al., 1996) and some plasticizers (Okubo et al., 2003) have been reported since 1990s. Surface water augmented by the secondary effluents was also reported to be anti-estrogenic (Vega-López et al., 2007). Stalter et al. (2011) also emphasized that conventional activated sludge treatment exhibited poor removal efficiency of anti-estrogenic activity in the wastewater. Wu et al. (2009) found that there was an increase of anti-estrogenic activity in the secondary effluents during chlorination.

To control the risk of potential ecological impacts and other problems including color and odor, reclaimed water treatment plants always adopt tertiary treatment. Ozonation as an effective tertiary treatment process is widely used in wastewater reclamation plants all over the world. Ozone is an active and strong oxidant that can easily react with the unsaturated chemical bonds in organics. Furthermore, it has also been reported that ozonation can convert large molecules into smaller ones and increase the ratio of the hydrophilic organic fractions in the reclaimed water (Gong et al., 2008).

It is also believed that ozonation can reduce micropollutants such as endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in reclaimed water and the precursors of disinfection by-products (DBPs) in drinking water (Westerhoff et al., 2005; Zhang et al., 2006; Hollender et al., 2009). Some by-products with high toxicity, however, were suspected to be generated during ozonation, such as bromo-trihalomethanes and haloacetic acids, N-nitrosodimethylamine (Andrzejewski et al., 2008; Hollender et al., 2009). Nevertheless, as to our knowledge, the effect of ozonation on the anti-estrogenic activity in reclaimed water is still unknown.

In our research, we assessed the removal efficiency of anti-estrogenic activity in secondary effluents during ozonation, and investigated the relation between changes of DOM character and anti-estrogenic activity.

2. Materials and methods

2.1. Sample collection and preparation

Secondary effluent samples used in our study were collected from three municipal wastewater treatment plants (WWTP) using anaerobic–anoxic–oxic process (AAO) and oxic–anoxic–anaerobic process (inverted AAO), respectively. Water samples, kept with ice, were immediately delivered to laboratory and were filtered through glass fiber filters with pore size of 0.45 μm to eliminate suspended solids, then adjusted to pH 2.0 with sulfuric acid and stored at 4 °C.

Two humic acid solutions were synthesized in laboratory. The humic acid products used were a SIGMA-ALDRICH Humic Acid product from Switzerland and a JINKE Chemical Research Institute Humic Acid product from China. For preprocessing, the humic acid was dissolved in ultra-pure water and filtered with 0.45 μm filters to obtain a solution with a dissolved organic carbon (DOC) concentration around 20 mg L^{-1}.

2.2. Water quality analysis

A SHIMADZU TOC-5000A analyzer was employed to measure the concentration of DOC. A SHIMADZU UV-2401PC UV-VIS recording spectrophotometer was used to measure UV absorbance. A XINRUI SD-9011 color analyzer was used to identify the color. The water quality of sample A, B, and C are shown in Table S1 in Supplementary Information. The information of the synthesized humic acid solutions D and E are shown in Table S2 in Supplementary Information.

2.3. Ozonation experiments

The ozonation experiments were operated in bench scale. The batch ozonation reactor as shown in Fig. S1 in Supplementary Information consisted of an ozone generator, ozone detectors, glass columns, flowmeters, dehydrators, etc. Ultra-pure oxygen was adopted as the feeding gas for the ozone generator, and the secondary effluents and the humic acid solutions were reacted with the aerated ozone in the glass columns. Both of the input and the exhaust ozone gas was dehydrated before going through ozone detectors to avoid the damage from steam to the ozone detectors.

The secondary effluents or synthesized humic acid solutions (4 L) were used to react with ozone in each batch. The contact time and ozone dose in the glass column was 5 min and 0–10 mg L^{-1}, respectively. After the 5-min reaction, the ozone generator was turned off, and ultra-pure oxygen was added into the column for another 10 min to drive the residual ozone away.