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# Removal of humic substances from reverse osmosis (RO) and nanofiltration (NF) concentrated leachate using continuously ozone generation-reaction treatment equipment

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ABSTRACT

Concentrated leachate from membrane treatment process, which contains large amount of difficult-to-degrade humic substances, can induce potential hazards to ecological environment. In this study, the concentrated leachates from reverse osmosis (RO) and nanofiltration (NF) were treated by continuous ozone generating-reaction integrated equipment, and the removal characteristics of humic substances were analyzed using gel filtration chromatography (GFC), excitation-emission matrix fluorescence spectroscopy (EEM), XAD-8 resin fractionation, and Fourier transform infrared spectroscopy (FTIR). The results of XRD-8 fractionation and $SUVA_{254}$ showed that the humic substances including humic acid (HA) and fulvic acid (FA), were effectively removed along with the breakdown of aromatic hydrocarbons and decrease in the degree of humification during the ozonation process. After 110 min of reaction, HA in both concentrated leachates was completely removed. GFC analysis indicated that both concentrated leachates had much broader distribution after the degradation. The high molecular weight (MW) organic matter was transformed into low molecular weight of <10 kDa. The majority of high MW organics in NF concentrate were converted to low MW molecules of 10 kDa–1 kDa, while those in RO concentrate were decomposed to small MW molecules of <1 kDa. The results of EEM analysis implied that the degradation of HA and FA led to a significant decrease in the fluorescence intensity. Though the effluent of two concentrated leachate did not meet the maximum allowable criterion for leachate direct or indirect discharge standard in China, the composition and properties of organic matters in concentrated leachate were changed significantly after entire ozonation reaction, which would be conducive to the further biological treatment or other advanced treatment.



## 1. Introduction

Stacking bales of municipal solid waste (MSW) and landfill produce leachate. During rains, rainy water, water from the biodegradation of MSW and the inherent waste of MSW get mixed. This mixture contains many hazardous substances in high concentrations (such as, COD, $NH_3$-N, and heavy metals) (Renou et al., 2008; Seo et al., 2007). The composition and properties of leachate vary with landfill age, types of landfill waste, climatic and hydrological conditions, and modes of operation (Chai et al., 2013, 2012; Chen et al., 2004). It is estimated that a ton of MSW with a moisture content of 30–35% will generate about 0.05–0.07 ton of leachate during the landfill process. The complexity and intractability of leachate treatment significantly increase with the age of landfill due to the presence of high concentrations of aromatic hydrocarbons, chlorinated aliphatics and humic substances (Chai et al., 2013; Wiszniowski et al., 2006).

Conventional aerobic and anaerobic biological treatment methods have been used as the main processes for leachate treatment because of their low cost and easy operation (Chan et al., 2009). In 2008, the direct effluent discharge criteria of leachate became stricter in China. To meet stringent effluent discharge standards, membrane treatment technologies, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis

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(RO), have widely been applied to advanced treatment of landfill leachate (Li et al., 2007; Dijk and Roncken, 1997; Yang et al., 2006). However, one of key problems in this method was the generation of large amount of concentrated leachate (retentate or reject water). For example, during NF and RO membrane process, as much as 13–30% of total incoming leachate was in the form of concentrated leachate. As a result, concentrated leachate contains high concentrations of pollutants and humic substances. Two of the major pollutants present in the concentrated leachate are humic acid (HA) and fulvic acid (FA), having percentages ranging from 61.7% to 75.0%. The contaminant in the concentrated leachate can induce biotoxicity. Sun et al. (2014) have indicated that RO concentrate can cause serious genotoxicity (1795.6 μg 4-NQO per liter) and antiestrogenic activity (2.19 mg TAM per liter). A recent report showed that with a half maximal effective concentration ($EC_{50}$) of 5.0 mg $L^{-1}$ (HA) and 44.7 mg $L^{-1}$ (FA), both HA and FA are toxic to organisms, as confirmed by the biotoxicity tests using luminescent bacteria (He et al., 2015a).

The main treatment technologies of concentrated leachate can be classified into four categories (He et al., 2015a,b; Hunce et al., 2012; Li et al., 2012; Perez-Gonzalez et al., 2012; Zhang et al., 2006): (1) recirculation to landfills; (2) solidification/stabilization; (3) evaporation/distillation; (4) advanced oxidation processes (AOPs) including Fenton oxidation, electrochemical oxidation, photocatalytic oxidation and ozonation ($O_3$). The recirculation of concentrated leachate to landfills may inhibit the microbial activity of methanogenesis due to its high concentrations of humic substances, heavy metals and inorganic salts (Calabro et al., 2010). The main drawbacks of evaporation/distillation treatment include high land utilization, high operating costs, poor stability and reliability, and equipment corrosion (Perez-Gonzalez et al., 2012). Among the four categories, AOPs is an attractive method to remove color, recalcitrant organics and to increase the biodegradability of concentrated leachate. Fenton process can effectively decompose organic matter via production of powerful oxidizing agents, such as hydroxyl radicals (·OH). However, it also has shortcomings such as the generation of a large amount of iron sludge (Deng and Englehardt, 2006).

Since ozone is a strong oxidant and is more effective for decomposing organics, therefore ozonation was reported to be used as an alternative approach in the treatment of leachate from sanitary landfills (Baig et al., 1999; Silva et al., 2004; Tizaoui et al., 2007). Oxidation of the pollutants can occur via oxidation effect of ozone or hydroxyl radicals (·OH) or through the combination of $O_3$ and ·OH (Von Gunten, 2003). With an oxidation potential ($E_0$) of 2.08 V, ozone can induce a direct electrophilic attack to decompose recalcitrant organics. Moreover, hydroxide ions can initiate ozone decomposition to yield ·OH with a high oxidation potential ($E_0$) of 2.80 V (Kurniawan et al., 2006). Moreover, ozonation process can alter the molecular structure of refractory organic substances, destroy recalcitrant compounds and improve biodegradability. A previous study showed that ozone-based treatment can achieve values of 73% and 62% for total average removal efficiencies of chemical oxygen demand (COD) and dissolved organic carbon (DOC) in leachate respectively (Bila et al., 2005). However, there are few studies about the application of ozone on the treatment of NF and RO concentrated leachate, as well as the treatment efficiency and removal characteristics of hard-degradable humic pollutants.

The objective of this study was to investigate the removal capacity and the study of degradation and transformation characteristics of humic substances in RO and NF concentrated leachate using a continuously ozone generating-reaction integrated equipment. In particular, the removal efficiencies of humic and non-humic fractions, and the changes in mean oxidation state (MOS) of organic carbon after ozone treatment were determined. Meanwhile, changes in organic molecular weight and fluorescence properties during ozonation process were monitored using gel filtration chromatography (GFC) and excitation-emission matrix fluorescence spectroscopy (EEM). In addition, after ozonation process, the effluent index of two concentrated leachate was compared with the maximum allowable criterion for leachate direct or indirect discharge standard in China. Finally, the degradation and transformation of humic substances in RO and NF concentrated leachate were evaluated by Fourier transform infrared spectroscopy (FTIR).

## 2. Materials and methods

### 2.1. Sample collection

Two kinds of concentrated leachate samples, NF concentrated leachate (NFC) and RO concentrated leachate (ROC), were collected from two different leachate treatment plants located in Qingdao, China. The treatment processes of two kinds of municipal waste leachate are listed in Fig. 1. NFC was collected from the leachate treatment plant of MSW transfer station, which was mainly responsible for the transportation of MSW from four districts (Shinan district, Shibei district, Licang district and part of Laoshan district) of Qingdao, China. The average transferred amount of MSW was 4000 tons $d^{-1}$. The scale of leachate treatment plant was 260 tons $d^{-1}$, mainly including 200 tons $d^{-1}$ of MSW leachate generated from the transportation process and 60 tons $d^{-1}$ of flushing wastewater, such as vehicles, equipment and ground. ROC was collected from the leachate treatment plant of Xiaojianxi MSW sanitary landfill. The total area of the landfill is about 1.6 $km^2$. The site has been in operation since 2002, which receives around 3300 tons $d^{-1}$ of the MSW. The plant was designed to treat leachate 900 tons $d^{-1}$, which was mainly (600 tons $d^{-1}$) from the landfill area and partly 300 tons $d^{-1}$ from the storage site of a MSW incineration plant. In this work, during NF and RO membrane process, the percentage of concentrated leachate in NFC and ROC were found to be 15.0% and 26.2%, respectively. Around 300 L of each concentrated leachate sample was collected on September 25, 2015. In order to minimize any changes in chemical and biological properties, the concentrated leachate samples were kept tightly sealed in a cool place (at 8–13 °C) until further use. The ozone experiments and water quality analysis were carried out within a week of sample collection. The chemical characteristics of two concentrated leachate samples are listed in Table 1. As seen from Table 1, the water quality of two samples was different. In leachate wastewater treatment process, it is difficult to obtain the same or similar water quality samples from RO and NF units, because the water quality of concentrated leachate was dependent upon many factors, including water quality of leachate, types of membrane materials, membrane pressure and fouling, and pretreatment and biological treatment stages of the leachate. Herein, without further treatment, the removal efficiencies of two different kinds of concentrated leachate are compared.

### 2.2. Ozone oxidation experiment

In the traditional ozone treatment process, $O_3$ gas was directly pumped into the wastewater treatment reactor. The contact efficiency between $O_3$ gas and dissolved pollutants could directly affect the removal efficiency of pollutants and the utilization of ozone gas. The contact time between $O_3$ gas and pollutants was usually very short, and the contact efficiency was quite low. Due to these factors, the pollutants removal efficiency of $O_3$ was found to be very limited. Moreover, the bubble size of $O_3$ gas affects the contact between the $O_3$ gas and pollutants. Unlike the traditional