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Effect of Fenton oxidation on biodegradability, biotoxicity and dissolved organic matter distribution of concentrated landfill leachate derived from a membrane process

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ABSTRACT

The treatment of concentrated landfill leachate from membrane process is a troublesome issue due to high concentrations of biorecalcitrant pollutants. In this study, the effect of Fenton process on dissolved organic matter (DOM) distribution (i.e. humic acid (HA), fulvic acid (FA) and hydrophilic fraction (HyI)), chemical forms of toxic organic compounds and metals, and their biotoxicity were investigated. In the concentrated leachate, toluene, ethylbenzene and chlorobenzene predominated in the HyI fraction, while phthalate esters (PAEs) were mainly absorbed on the HA and FA fractions. PAEs were more readily removed from the HA and FA fractions than that from the HyI fraction in the Fenton process. The complexing abilities of DOM varied with types of metal in the concentrated leachate. The biotoxicities of the DOM fractions to luminescent bacteria (*Photobacterium phosphoreum* T3 mutation) were HA > FA > HyI. The biotoxicities of the hydrophobic organic contaminants to luminescent bacteria were not obvious in the concentrated leachate due to their low concentrations. Metals might be the main contributor to the biotoxicity to luminous bacteria in the concentrated leachate. These results indicated that Fenton process could influence the pollutants distribution in DOM and their biotoxicities through the breakdown of HA and FA in the concentrated leachate.

1. Introduction

Pressure-driven membrane process (microfiltration, ultrafiltration, nanofiltration, reverse osmosis (RO)) is one of the most promising and efficient methods for landfill leachate treatment (Li et al., 2007, 2010). Large volume of concentrated leachate is generated from the pressure-driven membrane process separating into a purified permeate fraction and a concentrated retentate fraction, especially during the RO process. Normally, the concentrated retentate leachate produced from pressure-driven membrane process represents typically 13–30% of total incoming landfill leachate (Bruggen et al., 2003; Zhang et al., 2009; Calabrò et al., 2010). Concentrated leachate is a kind of brown solution with high chemical oxygen demand (COD) and low ratio of five-day biochemical oxygen demand (BOD_5) to COD (Calabrò et al., 2010). Recalcitrant organic matter including humic acid (HA), fulvic acid (FA), aromatic compounds, long-chain hydrocarbons and halohydrocarbons is abundant in concentrated leachate and poses potential hazards to the surrounding environment (Zhang et al., 2013). The treatment of concentrated leachate becomes a troublesome issue due to higher concentrations of recalcitrant organic matter, ammonia nitrogen, heavy metals, chlorinated organic and inorganic salts (Zhang et al., 2013).

Advanced oxidation processes (AOPs) involving the generation of the hydroxyl radical has a very high oxidation potential and is able to oxidize almost all organic pollutants (Morais and Zamora, 2005). AOPs have been demonstrated their high efficiency on the organic matter removal from the wastewater (Klavarioti et al., 2009; Sharma et al., 2014; Sirés et al., 2014). Nevertheless, AOPs aiming at complete mineralization might become extremely cost-intensive as a unique process because the highly oxidized end products formed during chemical oxidation tend to be refractory to total oxidation by chemical means (Mantzavinos and Psillakis, 2004). A significant reduction of overall leachate treatment cost could be obtained by the combination of AOPs with a biological process and/or with other physicochemical technologies (Morais and Zamora, 2005; Rivas et al., 2005; Primo et al., 2008).

Fenton process is one of the most common AOPs applied to the degradation of a great variety of industrial wastewaters, including pharmaceutical, textile, chemical, paper pulp, food processing, cork processing, oil shale semicoke leachate, landfill leachate (Bautista

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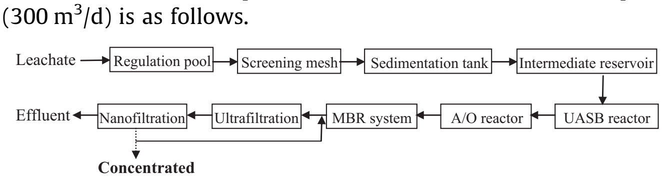
et al., 2008; Trapido et al., 2009). This technology is defined as the catalytic oxidation of organic compounds by hydroxyl radicals generated from the chain reaction between ferrous iron and hydrogen peroxide (Kang and Hwang, 2000; Neyens and Baeyens, 2003). Compared with other AOPs, Fenton process is simpler and easier to operate. Moreover, the reagents of Fenton process are readily available, easy to store and relatively safe to handle (Primo et al., 2008). Since the oxidation of organic matter completely to CO_2 becomes uneconomic, Fenton process has also been studied and applied to convert initially biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water (Mantzavinos and Psillakis, 2004; Lopez et al., 2004; Morais and Zamora, 2005; Barnes et al., 2007). Thus, this process has been mostly proposed as a pretreatment to reduce the toxicity and improve the biodegradability of the effluent for further biological treatment. However, the toxicity of some intermediates after Fenton process can be higher than that of the initial compounds (Zazo et al., 2005). For example, the toxicity of hydroquinone and p-benzoquinone, which are formed in Fenton oxidation of phenol, are several orders of magnitude higher than that of phenol (Santos et al., 2004). Concentrated landfill leachate from membrane process contains high concentrations of recalcitrant organic matter and metals (Zhang et al., 2013). The characteristics and toxicities of pollutants in concentrated landfill leachate after the pre-treatment of Fenton process are important for the selection of subsequent biological treatment. Presently, the treatability of raw landfill leachate by Fenton process has been widely investigated (Deng and Englehardt, 2006; Deng, 2007; Hermosilla et al., 2009; Wang et al., 2009). However, few studies have been conducted to investigate the distribution of pollutants including organic matter and metals in dissolved organic matter (DOM) in concentrated leachate after Fenton process.

In this study, Fenton oxidation was introduced to improve the biodegradability of the concentrated landfill leachate from membrane process, evaluated in terms of BOD_5/COD ratio. The effect of Fenton process on DOM distribution (i.e. HA, FA and hydrophilic fraction (HyI)), chemical forms of hydrophobic organic contaminants (HOCs) including toluene, ethylbenzene, chlorobenzene, and four kinds of phthalic acid esters (PAEs) (dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and dioctyl phthalate (DOP)), metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd and Pb) and As, as well as their biotoxicity were investigated.

2. Materials and methods

2.1. Sampling and Fenton process

The concentrated leachate sample used in this study was collected from a leachate membrane process of municipal solid waste landfill located in Zhejiang Province, China. The area and total storage capacity of the landfill are about 3.7×10^5 m^2 and 6.47×10^6 m^3, respectively. The age of the landfill is ~5 years. The landfill is active now. The ultrafiltration and nanofiltration membrane treatment is carried out after a biological treatment for the leachate. The process of the leachate treatment plant (300 m^3/d) is as follows.



The raw leachate sample was collected in the regulation pool and its characteristics were: pH, 7.65; COD, 2757 mg/L; BOD_5, 1034 mg/L. The concentrations of COD and BOD_5 of the concentrated leachate from membrane process were 3060 and 288 mg/L, respectively. Approximately 100 L concentrated landfill leachate sample was taken from the membrane process and stored at 4 °C for this study. The whole experiment was immediately run after collecting the concentrated leachate samples.

Fenton process was carried out in a 1000 mL beaker containing 400 mL of concentrated leachate sample at ambient temperature (~20 °C). Tests of single factor were run to study the optimal Fenton conditions for improving the biodegradability of concentrated leachate. (1) Effect of Fe^{2+} concentration on Fenton treatment was studied with the Fe^{2+} concentration ranging from 100 to 1000 mg/L at a initial pH of 3, H_2O_2/Fe^{2+} mass ratio of 9 and reaction time of 2 h; (2) Effect of pH on Fenton treatment was run within the pH range of 2–6.5 at a Fe^{2+} concentration of 400 mg/L, H_2O_2/Fe^{2+} mass ratio of 9 and reaction time of 2 h; (3) Effect of H_2O_2/Fe^{2+} mass ratio on Fenton treatment was investigated with the H_2O_2/Fe^{2+} mass ratio of 1–15 at a Fe^{2+} concentration of 400 mg/L, initial pH of 3 and reaction time of 2 h; (4) Effect of reaction time on Fenton treatment was investigated at a Fe^{2+} concentration of 400 mg/L, initial pH of 3 and H_2O_2/Fe^{2+} mass ratio of 9. The pH of the concentrated leachate was adjusted to 2.0, 3.0, 4.0, 5.0, 6.0 by HCl or NaOH solution. $FeSO_4 \cdot 7H_2O$ and 35% (w/w) of H_2O_2 solution were added to obtain the set dosage of Fe^{2+} and/or H_2O_2. The sample was magnetically stirred during reaction. At the end of Fenton process, the pH of the mixture was adjusted to 7.0–7.5. The concentrated leachate after the Fenton process was allowed to precipitate for 3 h, the supernatant was used for the following analysis. Each reaction was conducted in triplicate.

The optimal condition of Fenton process for the improvement of the BOD_5/COD ratio of the concentrated leachate was used to conduct the sequential experiment.

2.2. Biotoxicity analysis

DXY-2 Biotoxicity Analyzer and luminescent bacteria (*Photobacterium phosphoreum* T3 mutation)) (Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China) were used for biotoxicity analysis according to the GB/T 15441-1995 standard method (Chinese Environmental Protection Agency, 1995). Toxicity values were determined by DXY-2 Biotoxicity Analyzer when the bacteria were exposed to the tested compounds or wastewater in 3% NaCl solution for 15 min (Li et al., 2012; Chen et al., 2014). Median effective concentration (EC_{50}) was chosen as the indication to estimate the toxicity of the concentrated leachate before and after Fenton process, the aqueous phase obtained from DOM fractions, the organic compounds and metals. EC_{50} was obtained according to the method described by Wang et al. (2010).

2.3. Analytical methods

DOM in the concentrated leachate before and after Fenton process was fractionated into HA, FA and HyI fractions as the method described by Zhang et al. (2013). HOCs including toluene, ethylbenzene, chlorobenzene, DMP, DEP, DBP and DOP were analyzed in the concentrated leachate. The concentrated leachate before and after Fenton process and the aqueous phase obtained from DOM fraction were pre-treated using liquid–liquid extraction as follows. 150 mL sample was extracted with 20 mL diethyl ether for three times. The extract mixture was demulsified by centrifuging at 4000 rpm for 10 min. After dehydrated with anhydrous Na_2SO_4, the extract mixture was condensed to be nearly dry with a rotary evaporator, and then diluted to 0.5 mL with methanol for following analysis. Concentration of the organic compounds was determined using a gas chromatography (Tianmei, Shanghai, China) equipped with a capillary column (SE-54, 32 m × 0.32 mm × 1.5 μm) and flame