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Research article

Degradation behavior of dimethyl phthalate in an anaerobic/anoxic/oxic system

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A B S T R A C T

Dimethyl phthalate (DMP) as one of the most important and extensively used Phthalic acid esters (PAEs) is known to likely cause dysfunctions of the endocrine systems, liver, and nervous systems of animals. In this paper, the degradation and behavior of DMP were investigated in a laboratory scale anaerobic/anoxic/oxic (AAO) treatment system. In addition, a degradation model including biodegradation and sorption was formulated so as to evaluate the fate of DMP in the treatment system, and a mass balance model was designed to determine kinetic parameters of the removal model. The study indicated that the optimal operation condition of HRT and SRT for DMP and nutrients removal were 18 h and 15 d respectively, and the degradation rates of anaerobic, anoxic and aerobic zones for DMP were 13.4%, 13.0% and 67.7%, respectively. Under the optimal conditions, the degraded DMP was 73.8%, the released DMP in the effluent was 5.8%, the accumulated DMP was 19.3%, and the remained DMP in the waste sludge was 1.1%. Moreover, the degradation process of DMP by acclimated activated sludge was in accordance with the first-order kinetics equation. The model can be used for accurately modeling the degradation and behavior of DMP in the AAO system.

1. Introduction

In recent years, phthalic acid esters (PAEs) have caught extensive concerns because they are widely used as plastic plasticizers, and additives in more than hundred varieties of products, such as toy, packing material and cosmetics production. Therefore, these persistent and toxic organic compounds, which could harm the health of organisms and human by transmission of food chain and bioaccumulation, commonly exists in various environments (Latini, 2005; Magdouli et al., 2013). Dimethyl phthalate (DMP) known as one of the most important and extensively used PAEs, has been already measured in various environment, such as various surface water, groundwater, sediments of water, atmosphere, aerosol particle, soil (Wu et al., 2011; Huang et al., 2015; Montuori et al., 2008; Ogunfowokan et al., 2006; Zeng et al., 2009), and is known to likely cause dysfunctions of the endocrine systems, liver, and nervous systems of humans and animals (Wang et al., 2008; Yuan et al., 2008; Calafat and McKee, 2006; Wu et al., 2011). Therefore, DMP has been listed as a priority control pollutant by American Environmental Protection Agency (1991), Ministry of Environmental Protection of the People's Republic of China (Mohan et al., 2007) and European Union (1993).

The plasticizers in the water environment is mainly from discharge of industrial effluent without treatment. However, due to its persistence and refractory, the wastewater treated though the wastewater treatment plants (WWTP) is also an important source of The plasticizers in the water environment (Gao et al., 2014; Loraine and Pettigrove, 2006). When these toxic chemicals pass through the domesticated biological treatment process, which can overcome the shortcoming of traditional-activated sludge process, they are quite recalcitrant to be degraded and may direct discharge into the receiving water bodies. If PAEs are not removed at WWTP, there may be toxic or endocrine disrupting influences on aquatic organisms in the receiving water bodies (Knudsen and Pottinger,

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Abbreviation

PAEs	Phthalic acid esters
DMP	Dimethyl phthalate
WWTP	Wastewater treatment plants
AAO	Anaerobic/anoxic/oxic
COD	Chemical organic demand
BOD	Biochemical oxygen demand
TN	Total nitrogen
NH_4^+-N	Ammonium nitrogen
TP	Total phosphorus
DO	Dissolved oxygen
HRT	Hydraulic retention time
SRT	Sludge retention time
MLSS	Mixed liquor suspended solid
HPLC	High performance liquid chromatography
MAPE	Mean absolute percentage error
RMSE	Root mean squared error
SOM	Suspended organic matter

1999; Meghdad et al., 2009).

As such compounds are degraded slowly by photodegradation and hydrolyzation under natural conditions, biodegradation is thought of as one of the major degradation pathways for PAEs (Staples et al., 1997; Huang et al., 2011). Previous studies have demonstrated that several PAEs can take the biodegradation under aerobic conditions in activated sludge (Sanna et al., 2004; Cendrine et al., 2009), in soil and sediments (Peng and Li, 2012), in river, lake or sea water (Chen et al., 2009; Fang et al., 2009), and under anaerobic conditions (Liang et al., 2007; Wang et al., 2000), and the degradation rate of PAEs can reach from 60% to 100% though WWTP, which includes aerobic and anaerobic treatment zones (Gao et al., 2014; Oliver et al., 2005). From these studies it can be concluded PAEs could be effectively removed under aerobic conditions, but for anaerobic conditions, the degradation efficiency of PAEs becomes much slower (Huang et al., 2010; Mahmoud et al., 2012; Ruan and Xu, 2011). However, these studies have tended to pay attention to the biodegradability and degradation pathway of different PAEs.

Hence, the effective degradation of DMP in WWTP is essential to be understood so that the effluent concentration of DMP can be minimized to discharge into the receiving water bodies. Previous researches demonstrated that various PAEs have high biodegradation efficiency in the present of activated sludge (Kumar et al., 2014; Brar et al., 2009), and various PAEs could be removed by adsorption onto activated sludge. As a consequence, it is believable that the main removal mechanisms for DMP removal could be sorption on activated sludge and biodegradation. However, it is also very controversial and very challenging how these removal processes interacts with in WWTP.

Moreover, in order to describe the removal process of pollutants in WWTP and understand the degradation of pollutants in WWTP, many researchers focus on the kinetics of pollutants in WWTP (Meghdad et al., 2009; Patrik et al., 2003; Jarungwit et al., 2016). But in the previous study, the kinetic model is only used for modeling the biodegradation of PAEs, not take into account the fate of PAEs in WWTP. Thereby, it still needs to clearly investigate the degradation mechanism and behavior of DMP in the treatment system. And on this basis a model describing the degradation behavior of DMP should be built.

In this work, the degradation behavior of DMP were investigated in an anaerobic/anoxic/oxic (AAO) treatment system under various operating conditions. In order to evaluate the fate of DMP in the treatment system, three removal models including biodegradation and sorption process for anaerobic, anoxic and aerobic reaction were developed, respectively. In the end, a mass balance model based on degradation and behavior of DMP was designed to determine the kinetic parameters of the removal models.

2. Materials and methods

2.1. Reactor system

As shown in Fig. 1, the AAO treatment system made of polyethylene includes mainly four parts: one anaerobic zone with volume of 40 L, one anoxic zone with volume of 40 L, three aerobic zone with total volume of 160 L and one settling zone. there were two motor-driven stirrers employed in anaerobic and anoxic zones. An air blower was used to supply oxygen to the microorganisms of aerobic zone. The mixed liquor passing through the aerobic zones was recycled to the anoxic zone, and the sludge was returned from the bottom of the settling zone to the anaerobic zone. The reflux ratios of the mixed liquor and sludge were same, and set to 1. The pH of anaerobic digester is controlled at 6.5–8.0.

2.2. Feed

The sludge from a sewage treatment plant in Guangzhou was cultivated in a laboratory scale AAO treatment system with synthetic wastewater as feed. The synthetic wastewater with five different concentrations of DMP, which included 30, 40, 50, 60, and 80 μg L-1, was used. Chemical organic demand (COD) was supplied from glucose. Ammonium nitrate and potassium dihydrogen phosphate were added to maintain the nitrogen and phosphorous sources in the system. The ratio of COD:N:P was kept at 100:7:1.

2.3. Operation conditions of the experiment

In order to maintaining at a constant temperature of 25 °C, the work environment reactor system was controlled by the temperature control system. Dissolved oxygen (DO) was measured by the online dissolved oxygen meter (D53, HACH), and the concentrations of DO in anaerobic, anoxic and aerobic zones were within the scope of 0–0.30 mg L^{-1}, 0–0.60 mg L^{-1} and 2.54–5.72 mg L^{-1}, respectively. The mixed liquor suspended solid (MLSS) concentration of about 3000 mg L^{-1} was controlled. On the basis of changing the influent pump flow, hydraulic retention time (HRT) would be adjusted. Just as well sludge retention time (SRT) would be adjusted through altering the amount of the discharged excess sludge in the bottom of the settling zone. In order to investigate the influence of HRT and SRT on the degradation and behavior of DMP, different HRTs with 12, 18, 24, and 30 h and different SRT with 10, 15, 20, and 25 d were used. The continuous period of the operated system was one year.

2.4. Sampling and extraction

Water phase: in this work, the samples from the inlet and outlet of the reactor system and mixed liquors in anaerobic, anoxic and aerobic zones were filled into 1 L glass bottles once per day. Firstly, after all samples were treated by centrifugation at 3000 rpm for 15 min, 3% sulfuric acid was added to adjust pH of the supernatant at 3. And then a solid phase extraction column (Waters Oasis HLB, 200 mg/6 mL) was used to extract the centrifuged samples. When the flow rate of the supernatant flowing through the columns was up to 1–2 mL min^{-1}, the columns were washed with 3 mL