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Anaerobic degradation of dimethyl phthalate in wastewater in a UASB reactor

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ABSTRACT

Over 99% of dimethyl phthalate (DMP) and 93% of chemical oxygen demand (COD) were effectively removed in a continuous upflow anaerobic sludge blanket (UASB) reactor from a wastewater containing 600 mg/L DMP at 8 h of hydraulic retention time (HRT), corresponding to a loading rate of 3 g-COD/(L d). Each gram of sludge, expressed as volatile suspended solids (VSS), had a maximum specific methanogenic activity (SMA) of 24 mg-CH_4/(g-VSS d) using DMP as the sole carbon source. The sludge yield was estimated as 0.08 g-VSS/g-COD. During anaerobic degradation, DMP was de-esterified, first to mono-methyl phthalate (MMP) and then to phthalate, before being de-aromatized and subsequently converted to CH_4 and CO_2. The maximum specific degradation rates of DMP, MMP and phthalate were 415, 88 and 36 mg/(g-VSS d), respectively. Analysis based on polymerase chain reaction (PCR) and denaturing gradient gel electrophoresis (DGGE) showed a gradual shift of microbial population with the increase of DMP loading.

1. Introduction

Phthalic esters (PEs) are a group of chemicals widely used as additive in the manufacturing of plastics. They are listed as priority pollutants in many countries due to their suspected mutagenicity and endocrine disrupting effects. Since PEs are not chemically bound to the host plastics, they are inevitably leached from the products and released to the environment ultimately. They have been detected in surface water, wastewater, sewage sludge and sediment (Fromme et al., 2002), as well as landfill leachate (Marttinen et al., 2003).

PEs can be biodegraded in surface waters, soils and sediments under various conditions, either aerobic, anoxic (Liang et al., 2007) or anaerobic (Staples et al., 1997). Of all PEs, dimethyl phthalate (DMP) is the simplest and the most commonly used. Although DMP has only a moderate toxicity with a LD_{50} of over 5 mL/kg for rats (Autian, 1973), its metabolite mono-methyl phthalate (MMP) is not only toxic but also an endocrine disruptor, i.e. MMP may interfere with the development and reproductive system of animals, or even human, by reducing testosterone production and decreased sperm counts (Lottrup et al., 2006). Under aerobic conditions, DMP in wastewater could be effectively removed in batch reactors in less than 5 days at the initial concentration of 400 mg/L (Wang et al., 2003, 2004) as well as in continuous packed-bed reactors at a volumetric rate of 560 mg/(L h) (Juneson et al., 2002). Under anoxic conditions, DMP could be degraded at the rate of 62 mg/(g-VSS h) (Liang et al., 2007). Its degradation under anaerobic conditions is, however, much slower. Batch data show that it required 7 days to degrade DMP using a digester sludge (Shelton et al., 1984), 17 days using a sludge obtained from an upflow anaerobic sludge blanket (UASB) reactor (Kleerebezem et al., 1999), and up to 70 days in a laboratory-scale municipal solid waste landfill (Ejlertsson et al., 1996). Most anaerobic studies of PEs degradation so far were conducted in batches. Little information is available on the degradation of DMP in wastewater in continuous flow reactors.

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This study was conducted to investigate the anaerobic degradation of DMP in wastewater using a UASB reactor under mesophilic condition. The effect of using phenol as a co-substrate during startup for enhancing the microbial biodegradability was evaluated. The maximum loading rate, degradation intermediates, and the specific methanogenic activity (SMA), as well as the microbial population of the DMP-degrading sludge, based on denaturing gradient gel electrophoresis (DGGE) (Muyzer et al., 1993) analysis of extracted DNA, were also investigated.

2. Material and methods

2.1. DMP degradation in a UASB reactor

A 2.8-L UASB reactor (Fang et al., 1996) was used for treating a synthetic DMP-containing wastewater at 37 °C for over 530 days. It was operated with an effluent-recycling ratio of 1:1 in order to reduce the toxic effect of DMP. The reactor was seeded with the phenol-degrading sludge from a previous study (Fang et al., 1996), in which phenol was effectively degraded at concentrations up to 1260 mg/L. For each gram of theoretical oxygen demand, the feed solution consisted of following nutrients: 1 g $NaHCO_3$, 200 mg NH_4Cl, 42.5 mg $MgSO_4 \cdot 7H_2O$, 24.8 mg K_2HPO_4, 9.9 mg KH_2PO_4, 13.0 mg $CaCl_2$, 5.3 mg $NiSO_4 \cdot 7H_2O$, 4.1 mg $FeCl_3 \cdot 6H_2O$, 1.1 mg $MnCl_2 \cdot 4H_2O$, 0.6 mg $ZnCl_2$, 0.6 mg $CoCl_2 \cdot 2H_2O$, 0.4 mg $(NH_4)_2MoO_4 \cdot 4H_2O$, 0.3 mg $CuCl_2 \cdot 2H_2O$ and 0.2 mg $NaBO_2 \cdot 10H_2O$. The 530-day operation was divided into two stages, depending on whether phenol was used as co-substrate. The operational conditions are summarized in Table 1.

In Stage I (Days 1–232), phenol with decreasing concentrations was used as the co-substrate allowing the sludge a gradual acclimation to DMP. The reactor was started by feeding an influent containing DMP/phenol at respective concentrations of 300/1050 (both in mg/L), corresponding to a chemical oxygen demand (COD) loading of 3000 mg/L. The hydraulic retention time (HRT) was kept at 20 h, after a brief period operating at 12 h at which the effluent COD exceeded 400 mg/L. Afterwards, the DMP/phenol concentrations (in mg/L) were changed stepwise from 300/1050 to 600/840, and then to 800/630, once the COD removal efficiency reached 90% at the given concentration levels. However, when DMP/phenol concentrations at 800/630 (mg/L), the COD removal dropped below 75% and could not recover after several weeks. By changing the concentrations back to 600/840 mg/L, COD removal efficiency was gradually recovered and was kept steady over 90% for the next 50 days.

In Stage II (Days 233–530), phenol was removed from the influent. DMP was kept at 600 mg/L, equivalent to 1000 mg-COD/L, as the sole carbon source. Similar to Stage I, once the COD removal efficiency reached 90%, the organic loading was increased by lowering the HRT stepwise from 20 h to 16, 12, 9.6 and lastly 8 h.

2.2. Specific methanogenic activity (SMA)

The SMA of DMP-degrading sludge at 37 °C was conducted in 282 mL serum bottles in batch mode. The SMA is an indicator of the methanogenic activity of the biomass under a condition in which the supply of substrate is not a limiting factor. Seed sludge was sampled from the DMP-degrading UASB reactor at the end of Stage II on Day 530, when the reactor was operated at 3 g-COD/(L d) removing 100% of DMP and 93% of COD from the influent. In each batch test, the initial sludge concentration, measured as volatile suspended solids (VSS), was 900 mg/L. Substrates in the SMA tests were DMP and eight possible degradation intermediates, including formate, acetate, propionate, butyrate, caproate, benzoate, phenol and phthalate. The initial concentration of each substrate was chosen to ensure that substrate supply was not the limiting factor and yet without causing an inhibitory effect. Initial concentrations of DMP varied from 100 to 1500 mg/L at six levels. Initial concentrations for other substrates were (in mg/L): formate 4320, acetate 1400, propionate 990, butyrate 825, caproate 490, benzoate 505, phenol 420, and phthalate 690. These concentrations were equivalent to 1500 mg-COD/L for the first four substrates, and 1000 mg-COD/L for the others.

2.3. Chemical analysis

In each SMA test, biogas production and composition, DMP and its metabolites, including volatile fatty acids (VFAs), were

Table 1 – Operation conditions of anaerobic DMP degradation in the UASB reactor

Stage	Time (d)	HRT (h)	DMP (mg/L)	Phenol (mg/L)	COD (mg/L)	DMP loading (mg/(L d))
I	1–57	12	300	1050	3000	600
	58–89	20	300	1050	3000	360
	90–110	20	600	840	3000	720
	111–177	20	800	630	3000	960
	178–232	20	600	840	3000	720
II	233–322	20	600	–	1000	720
	323–355	16	600	–	1000	900
	356–372	12	600	–	1000	1200
	373–400	9.6	600	–	1000	1500
	401–530	8	600	–	1000	1800