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Anaerobic biodegradation of 8:2 fluorotelomer alcohol in anaerobic activated sludge: Metabolic products and pathways

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HIGHLIGHTS

- 8:2 FTOH biodegradation can be well described by a double exponential decay model.
- 8:2 FTUA and PFOA were the most abundant poly- and perfluorinated metabolites.
- All polyfluorinated metabolites could be further transformed.
- PFPeA and PFBA were first detected during anaerobic biodegradation of 8:2 FTOH.

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ABSTRACT

The anaerobic biodegradability and metabolic pathways of 8:2 fluorotelomer alcohol (8:2 FTOH) were investigated in anaerobic activated sludge. The biodegradation was well described by a double exponential decay model. 8:2 FTOH was biodegraded to poly- and perfluorinated metabolites with the release of fluoride ion. All polyfluorinated metabolites were intermediate metabolic products and could be further transformed to other metabolites, while perfluorinated metabolites were terminal products. 2H-perfluoro-2-decenoic acid (8:2 FTUA) and perfluorooctanoic acid (PFOA) were verified as the most abundant poly- and perfluorinated metabolites, respectively. Two shorter-chain perfluorinated metabolites, perfluoropentanoic acid (PFPeA) and perfluorobutyric acid (PFBA), were first reported in the biodegradation of 8:2 FTOH. However, the total molar recovery of 8:2 FTOH decreased with increasing incubation time, indicating that there might be some unknown metabolites. Thus, the anaerobic biodegradation pathways were proposed as follows: 8:2 FTOH was oxidized to 8:2 FTUA and 2-perfluorooctyl ethanoic acid (8:2 FTCA) via 2-perfluorooctyl acetaldehyde (8:2 FTAL), and then 8:2 FTUA and 8:2 FTCA were further transformed to 1-perfluoroheptyl ethanol (7:2 sFTOH) via 3-perfluoroheptyl propionic acid (7:3 acid) or/and 3-perfluoroheptyl acrylic acid (7:3 Uacid), and eventually 7:2 sFTOH was further biodegraded to PFOA and other perfluorocarboxylates containing less than eight carbons.

1. Introduction

The increasing release of perfluorocarboxylic acids (PFCAs) to natural environments and ecosystems over the last decades has spurred growing environmental and toxicological concerns because of their toxicity, bioaccumulation and persistence (Banzhaf et al., 2017; Rappazzo et al., 2017; Jian et al., 2017). The occurrence of PFCAs can be attributed to direct release from industrial manufacturing processes, product use and disposal, or generation from the indirect transformation, abiotic and biotic, of polyfluoroalkyl precursor chemicals, such as fluorotelomer alcohols (FTOHs, $F(CF_2)_{2n}CH_2CH_2OH$, $n = 2–8$). FTOHs are the commonly used materials to make polymeric and surfactant products with unique properties due to their highly fluorinated structure (Kissa,

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2001; Fasano et al., 2009; Chen et al., 2017; Yu et al., 2018). Although FTOH are volatile and can be easily transported in the environment, previous studies found that FTOH can also be degraded to PFOA and hence may cause the detection of PFOA in remote locations (Ellis et al., 2004; Wallington et al., 2006; Stock et al., 2007). Thus, to better comprehend the environmental fate of these fluorotelomer-based substances, it is essential to understand their biodegradability and biodegradation pathways under different environmental conditions.

Although chemical degradation of 8:2 FTOH ($C_8F_{17}CH_2CH_2OH$, the most commercially important FTOH) has been reported through either oxidation in the atmosphere (Ellis et al., 2004; Wallington et al., 2006; Stock et al., 2007) or photolysis in aqueous environments (Gauthier and Mabury, 2005), microbially catalyzed transformations of 8:2 FTOH also play important roles in different biological compartments, such as aerobic and anaerobic biodegradation in terrestrial environments (Dinglasan et al., 2004; Wang et al., 2005a,b, 2009; Liu et al., 2007; Kim et al., 2012; Yu et al., 2018). Biodegradation of per- and polyfluoroalkyl substance, including FTOH, was proposed to contribute to the increasing levels of PFOA and PFOS in sewage sludge (Higgins et al., 2005), effluents (Arvaniti and Stasinakis, 2015; Chen et al., 2017; Dauchy et al., 2017), and sediment (Higgins et al., 2005; Campo et al., 2016), landfill leachate (Allred et al., 2015; Lang et al., 2016), and biosolid applied soils and lands (Lee et al., 2013; Liu et al., 2017). Previous studies have examined the biodegradation of 8:2 FTOH and possible metabolic pathways and products under aerobic conditions in pure or mixed bacterial cultures (Dinglasan et al., 2004; Wang et al., 2005a,b; Kim et al., 2012), soil and sediment (Liu et al., 2007; Wang et al., 2009), activated sludge (Wang et al., 2005a,b) and brackish water (Keränen et al., 2013). However, very few studies have been conducted to investigate the anaerobic biodegradation of 8:2 FTOH. And most important, these results are inconsistent on the anaerobic biodegradability of 8:2 FTOH. Sáez et al. (2008) reported that 8:2 FTOH was not biodegradable in anaerobic activated sludge, while Zhang et al. (2013) found that 8:2 FTOH can be biodegraded to form poly- and perfluorinated products (e.g., fluorotelomer carboxylic acids to PFCAs) and release fluoride ion by anaerobic digester sludge under methanogenic conditions.

Therefore, better understanding of the biodegradability of 8:2 FTOH and possible biodegradation pathways and products under anaerobic conditions is essential to illustrate the fate and transport in diverse environments. Given that bacteria can biodegrade FTOH via different metabolic pathways (Kim et al., 2012), the metabolic products of 8:2 FTOH under anaerobic conditions may be different from that under aerobic conditions because of distinct microbial communities. Additionally, it is unknown whether alternative metabolic pathways exist to remove some of the $-CF_2-$ groups from 8:2 FTOH under anaerobic conditions.

The objectives of this study were to evaluate the biodegradability of 8:2 FTOH in anaerobic activated sludge, determine the anaerobic metabolite yields, and elucidate the biodegradation pathways. Furthermore, some potential metabolites of 8:2 FTOH, including 2-perfluorooctyl ethanoic acid (8:2 FTCA), 2H-perfluoro-2-decenoic acid (8:2 FTUA), 3-perfluoroheptyl propionic acid (7:3 acid), and 1-perfluoroheptyl ethanol (7:2 sFTOH), were also investigated for their anaerobic biodegradation metabolites and pathways under the same conditions.

2. Materials and methods

2.1. Standards and chemicals

8:2 FTOH (98%) was acquired from Sigma-Aldrich (Milwaukee, WI, USA). 8:2 FTCA (>98%, in isopropanol, 50 ± 2.5 μg/mL), 8:2 FTUA (>98%, in isopropanol, 50 ± 2.5 μg/mL), 7:3 acid (>98%, in methanol, 50 ± 2.5 μg/mL), 7:2 sFTOH (>98%, in methanol, 50 ± 2.5 μg/mL), perfluoro-[1,2,3,4−$^{13}C_4$]octanoic acid (MPFOA, >99%, in methanol, 50 ± 2.5 μg/mL, linear, >99% 1,2,3,4−$^{13}C_4$) and 2-perfluorooctyl-[1,1−$^2H_2$]-[1,2−$^{13}C_2$]-ethanol (8:2 MFTOH, >98%, in methanol, 50 ± 2.5 μg/mL, >99% 1,1−$^2H_2$ and 1,2−$^{13}C_2$) were obtained from Wellington Laboratories (Ontario, Canada). Perfluorononanoic acid (PFNA, 97%), perfluorooctanoic acid (PFOA, 96%), perfluoroheptanoic acid (PFHpA, 99%), perfluorohexanoic acid (PFHxA, ≥97%), perfluoropentanoic acid (PFPeA, 97%), perfluorobutyric acid (PFBA, 98%) and pentafluoropropionic acid (PFPrA, 97%) were purchased from Sigma-Aldrich, while trifluoroacetic acid (TFA, Analytical Standard) was obtained from Fluka (Buchs, Switzerland).

HPLC grade methanol (≥99.9%) and acetonitrile (≥99.9%) as well as BioXtra grade sodium fluoride (≥99%) were purchased from Sigma-Aldrich, while HPLC grade ammonium acetate (≥99.0%) and bulk Envi-Carb graphitized carbon sorbent (100 m^2/g, 120/400 mesh) were acquired from Fluka and Supelco (Bellefonate, PA, USA), respectively. Oasis® WAX cartridges (6 cc, 150 mg, 30 μm) were purchased from Waters (Milford, MA, USA). All the other inorganic compounds were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), unless other specifics were mentioned. Milli-Q water (Milli-Q® Reference, Merck Millipore, Germany) was used in this study.

2.2. Collection and pretreatment of anaerobic sludge

The anaerobic activated sludge used in this study was collected from an anaerobic tank in a municipal wastewater treatment plant (WWTP) located in Xiamen, China. This WWTP employs anaerobic-anoxic-aerobic processes with a designed treatment capacity of 4.5×10^4 m^3/d and the mixture ratio of industrial and domestic wastewater is around 4:6. Fluorine-containing organic compounds, including FTOH, fluorotelomer acid, perfluorocarboxylates, perfluoroalkylsulfonates, etc., were detected at ppb level in the WWTP influent because some small fluorochemical manufacturing and semiconductor etching facilities are located in the WWTP service area. The pH value, conductivity, and redox potential (ORP) of the collected sludge were measured at 7.5, 1250 μS/cm, and −200 mV, respectively.

The anaerobic sludge was collected in 1-L polypropylene (PP) wide-mouth bottles to the rim and immediately sealed with lids, and transported to the laboratory within 2 h. The sludge was treated with following procedures in an anaerobic chamber filled with nitrogen. The sludge was flushed with ultra-pure nitrogen (>99.999%) for 1 h and then allowed to settle down for 30 min. The supernatant was discarded and the concentrated sludge was filtered with qualitative filter paper (Φ15 cm, 15–20 μm, Whatman, GE, Hangzhou, China). And then the filtered sludge was rinsed thoroughly with oxygen-free water and then mixed using a vortex stirrer (Lab dancer, IKA, Staufen, German). The procedure of filtration followed by rinsing and mixing was repeated twice to remove potential interference substances as much as possible. Finally, the treated sludge was re-suspended in oxygen-free nutrient medium with an initial pH of ~7.5 and a final suspended solid (SS) concentration of ~20000 mg/L. The nutrient medium was prepared according to the recipe reported by Zhang et al. (2013), except the addition of 5.0 mg/L vitamin B_{12} (VB_{12}) as biocatalyst for dehalogenation, and its detailed compositions were listed in Table S1 in Supplementary Materials.

2.3. Biodegradation of 8:2 FTOH

Batch experiments of biodegradation were conducted in the