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Enhanced generation of perfluoroalkyl carboxylic acids (PFCAs) from fluorotelomer alcohols (FTOHs) via ammonia-oxidation process

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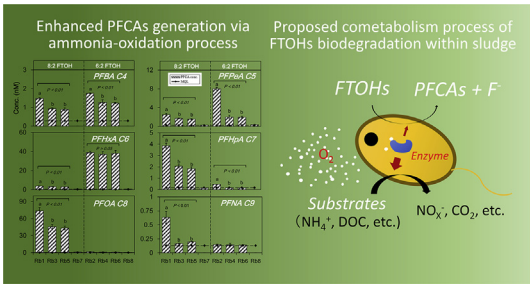
HIGHLIGHTS

- Cometabolism process influenced PFCAs generation from FTOHs in activated sludge.
- Generation of PFCAs and F^- correlated negatively with ammonia addition amounts.
- Ammonia-oxidation bacteria played an essential role in enhanced PFCAs generation.
- Ammonia monooxygenases may be incorporated in FTOHs biodegradation.

GRAPHICAL ABSTRACT



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ABSTRACT

With the phase-out of persistent, bioaccumulative, and toxic perfluoroalkyl carboxylic acids (PFCAs), it is needed to explore the potential release of PFCAs from precursors being emitted into the environment. Biotransformation of fluorotelomer alcohols (FTOHs) via biological processes in wastewater treatment plants (WWTPs) leads to discharge of PFCAs into receiving waters. However, the commonly existed microbial activity that can impact on FTOHs biodegradation in WWTPs remains unclear. The objective of present research was to explore the relationship between ammonia-oxidation process and the enhanced PFCAs generation from FTOHs biodegradation under aerobic activated sludge. The obtained results indicate that the cometabolism process performed by nitrifying microorganisms (NMs) was responsible for enhanced PFCAs generation. Among NMs, the ammonia-oxidation bacteria that can express non-specific enzyme of ammonia monooxygenases resulted in the enhanced PFCAs generation from FTOHs. Meanwhile, the different addition amount of ammonia contributed to different defluorination efficiency of FTOHs. The present study further correlated the enhanced PFCAs generation from FTOHs biodegradation with ammonia-oxidation process, which can provide practical information on effective management of PFCAs generation in WWTPs.

1. Introduction

Per- and polyfluorinated alkyl substances (PFASs) have been manufactured for wide application over the past 60 years (Lindstrom et al., 2011). Since 2000, their problematic properties of persistence, bioaccumulation, and toxicity have raised global concerns (Giesy and Kannan, 2001). The perfluoroalkyl carboxylic acids (PFCAs), which are one group of PFASs, have been universally distributed in the environment. Among PFCAs, perfluorooctanoic acid (C_8, PFOA) is recognized as probably carcinogenic to humans (Steenland et al., 2010; Vieira et al., 2013; White et al., 2011). In January 2006, the US Environmental Protection Agency initiated a

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global program to eliminate long-chain PFCAs including PFOA (US EPA, 2006). Recently, PFOA is being evaluated as a persistent organic pollutant candidate (Convention, 2015). While the manufacture of PFCAs has been largely restrained due to the awareness of their environmental risks, PFCAs still remain a moving target as PFCAs are continuously generated from numerous precursor compounds (Xiao, 2017). Accordingly, the clarification on transformation properties of precursors is essential to prevent the contamination expansion of PFCAs.

The domestic and industrial wastewaters are collected and treated in wastewater treatment plants (WWTPs) wherein PFCAs are frequently detected (Houtz et al., 2016; Xiao et al., 2012; Yu et al., 2016). Generally, PFCA concentrations in effluent are higher than those in influent (Eriksson et al., 2017). The increased effluent PFCAs are considered to derive from biodegradation of precursors such as fluorotelomer alcohols (FTOHs) (Loganathan et al., 2007; Yu et al., 2009), which are typical precursors that can degrade to PFCAs via biotic and abiotic pathways (Butt et al., 2014; Dinglasan et al., 2004; Ellis et al., 2004; Wang et al., 2005a, 2005b). Published studies have documented FTOHs biodegradation within sludge (Dinglasan et al., 2004; Wang et al., 2005a, 2005b; Zhang et al., 2013). One recent work provides field observations for FTOHs biodegradation and PFCAs generation in WWTPs (Chen et al., 2017). While those studies focus on exploring the biodegradation pathway, identifying the biotransformation products, and surveying the contamination status of FTOHs in sludge, the knowledge gaps still exist on understanding biotransformation of FTOHs under the commonly found conditions in activated sludge. Since the release of PFCAs from WWTPs will be associated with human exposure in the environment, the clarification on FTOHs biodegradation in WWTPs is expected to help to control PFCAs generation during biological treatment processes to reduce their release risks. We suggest that knowing the relevant functional microbial groups that are capable of FTOHs biodegradation can provide practical information for seeking suitable biological approaches to manage PFCAs generation in WWTPs.

Our former studies have investigated the effects of aerobic/anoxic/anaerobic conditions on 8:2 FTOH biodegradation in activated sludge. It was observed that rapid biodegradation of 8:2 FTOH and more generation of PFCAs achieved under aerobic condition (Yu et al., 2016). Then, we further revealed that the aerobic microorganisms using ammonia as substrate generated more PFCAs from FTOHs than using glucose as substrate (Yu et al., 2018). These observations suggest the high possibilities that the nitrifying microorganisms (NMs), which contain ammonia-oxidation bacteria (AOB) and nitrite-oxidizing bacteria (NOB), were involved in enhanced PFCAs generation from FTOHs biodegradation in aerobic activated sludge process. As it has been well-known that the AOB in activated sludge can not only metabolize ammonia but also cometabolize a wide range of micropollutants (Fernandez-Fontaina et al., 2012; Men et al., 2017; Xu et al., 2016), in this study, to extend on our previous observation, we propose the hypothesis that enhanced PFCAs generation from FTOHs biodegradation under aerobic condition is associated with cometabolism process performed by AOB in sludge.

In this context, the object of the present research was to explore the relationship between ammonia-oxidation process and the enhanced PFCAs generation from FTOHs. To achieve the objective, the following experiments were performed. Firstly, we examined PFCAs generation property in activated sludge with substrate of ammonia and glucose under their different concentrations. The aim was to understand the effects of cometabolism process of NMs and heterotrophs on PFCAs generation (Experiment-1). Secondly, as mentioned above, NMs mainly contain AOB and NOB; hence, the experiment was conducted to detail the role of AOB and NOB on enhanced PFCAs generation (Experiment-2). Finally, since defluorination can reflect FTOHs biodegradation, the investigation on estimating FTOHs defluorination under nitrification process was carried out (Experiment-3).

2. Materials and methods

2.1. Chemicals

Information about chemical names, acronyms, and structures of PFASs analyzed or described in the present study is elucidated in Table S1 (Supplementary Information, SI). The FTOH reagents were purchased from Tokyo Chemical Industry (Tokyo, Japan). A mixed standard solution (PFAC-MXB) used for quantifying PFCAs including perfluorobutanoic acid (C_4, PFBA), perfluoropentanoic acid (C_5, PFPeA), perfluorohexanoic acid (C_6, PFHxA), perfluoroheptanoic acid (C_7, PFHpA), PFOA, and perfluorononanoic acid (C_9, PFNA) was purchased from Wellington Laboratories Japan Inc. (manufactured in Guelph, Canada). The mass-labeled PFCAs surrogate (MPFAC-MXA) and the syringe spike of perfluoro-n-[$^{13}C_8$] octanoic acid (M8PFOA) were also purchased from the Wellington Laboratories Japan Inc. The other organic media for sample pretreatment and inorganic chemicals for artificial wastewater preparation are described in Table S2. Ultra-pure water (UPW) was generated by a MicroPure system UV/UF (Thermo Scientific, Thermo Electron LED GmbH, Langenselbold, Made in Hungary) and had a resistivity of >18.20 MΩ cm^{-1}. All the glassware and polypropylene (PP) centrifuge tubes were prewashed in methanol, rinsed in UPW, and dried in an oven at 80 °C. Teflon contained-materials were not used in the present study.

2.2. Activated sludge collection and culture preparation

The activated sludge (suspended solids, SS: 3.5 ± 0.3 g L^{-1}, $n = 8$) used in the present research was collected from the return sludge basin of a domestic WWTP in Kyoto, Japan. Before experiment, the sludge was aerated with ambient air for one day to deplete the remaining biodegradable dissolved organic compounds and ammonia. After the aeration treatment, the sludge was washed with phosphate buffer solution (pH 7.2). The concentrations of dissolved organic carbon (DOC) and nitrate (NO_3^-) in the supernatant of the last wash were less than 1 mgC L^{-1} and 0.5 mgN L^{-1}, respectively. The washed sludge was suspended in artificial wastewater, which was prepared with UPW containing 21.8 mg L^{-1} K_2HPO_4, 8.5 mg L^{-1} KH_2PO_4, 44.6 mg L^{-1} $Na_2HPO_4 \cdot 12H_2O$, 27.5 mg L^{-1} $CaCl_2 \cdot 2H_2O$, 22.5 mg L^{-1} $MgSO_4 \cdot 7H_2O$, and 0.25 mg L^{-1} $FeCl_3 \cdot 6H_2O$.

2.3. Experimental set-up

In present research, all the experiments were performed under aerobic condition. In order to prevent the volatile loss of FTOHs and their biotransformed products, the closed-bottle experimental systems were adopted. Meanwhile, to maintain the aerobic conditions in closed environments, the pure oxygen gas was used to aerate the sludge and exchange with the air in headspace of the reactors. This experiment system has been applied in our previous research (Yu et al., 2018).

2.3.1. Influence of NMs and heterotrophic activity on FTOH biodegradation (Experiment-1)

The 1.0 L pure-oxygen-aerated sludge was poured into a beaker, and 10 μL of 8:2 FTOH stock solution (50 mg mL^{-1}, dissolved in methanol) was dosed using a gas-tight syringe. The sludge was then homogenized by mixing for 10 min. After that, pH in the