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Factors controlling the rate of perfluorooctanoic acid degradation in laccase-mediator systems: The impact of metal ions☆

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ABSTRACT

This study investigated the factors that regulated the degradation of perfluorooctanoic acid (PFOA) in laccase-catalyzed oxidative humification reactions with 1-hydroxybenzotriazole (HBT) as a mediator. The reaction rates were examined under conditions with key factors varied, including initial PFOA concentrations, laccase and HBT dosages, and the ionic contents of the reaction solutions. The PFOA degradation followed pseudo-first order kinetics, and the rate constants (k) were similar for the high (100 μmol L^{-1}) and low (1.00 μmol L^{-1}) initial PFOA concentrations, respectively at 0.0040 day^{-1} ($r^2 = 0.98$) and 0.0042 day^{-1} ($r^2 = 0.86$) under an optimum reaction condition tested in this study. The metal ions contained in the reaction solution appeared to have a strong impact on PFOA degradation. Differential UV-Vis spectrometry revealed that Cu^{2+} can complex with PFOA, which plays an essential role to enable PFOA degradation, probably by bridging the negatively charged PFOA and laccase, so that the free radicals of HBT that are released from laccase can reach and react with PFOA. It was also found that Fe^{3+} plays a similar role as Cu^{2+} to enable PFOA degradation in the laccase-HBT reaction system. In contrast, Mg^{2+} and Mn^{2+} cannot complex with PFOA under the investigated conditions, and do not enable PFOA degradation in the laccase-HBT system. Fluoride and partially fluorinated compounds were detected as PFOA degradation products using ion chromatography and high resolution mass spectrometry. The structures of the products suggest the reaction pathways involving free-radical initiated decarboxylation, rearrangement, and cross-coupling.

1. Introduction

A large quantity of perfluorooctanoic acid (PFOA) had been produced to meet the massive demand in various important industrial applications such as surfactant, fire retardant, and surface treatment (Paul et al., 2008; Prevedouros et al., 2006). The wide applications of PFOA are attributed to its extreme thermal and chemical stability as well as its hydrophobic and hydrophilic nature (Guo et al., 2008). These physical-chemical properties are derived from the unique structural feature of PFOA in which all hydrogens in the carbon-carbon skeleton are replaced by fluorines (O'Hagan, 2008). PFOA enters the environment primarily through emission from manufacturing facilities (Armitage et al., 2006), utilization of PFOA-based products (Ahrens, 2011), and transformation from polyfluoroalkyl precursors (Ruan et al., 2015). PFOA is prevalent in soil, groundwater, surface water, and sediment. The occurrence of PFOA in the Arctic ocean with limited anthropogenic impact has been reported at levels ranging from 3 to 259 pg L^{-1} (Benskin et al., 2012). Relatively high concentrations of PFOA are frequently observed near manufacturing plants, disposal sites, and fire-fighting training areas. For example, the groundwater collected from the firefighting training areas where the aqueous film-forming foams (AFFFs) were applied contained up to 219 μg L^{-1} of PFOA (Backe et al., 2013).

PFOA has drawn tremendous attention from both the public and the scientific community due to its potential adverse effects on

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human health and the environment (Renner, 2001). The potential health risks from exposure to PFOA include hepatic, reproductive, developmental, immunological, and endocrine system toxicity (Lau et al., 2007; Spachmo and Arukwe, 2012). In 2008, the European Food and Safety Authority has established a tolerable daily intake value for PFOA of 1.50 μg kg^{-1} body weight (EFSA, 2008). Numerous studies have been devoted to developing treatment and remediation techniques for PFOA contamination. Techniques such as electrochemical, photolytic, and sonochemical oxidation either involve high energy inputs or require special devices to achieve effective PFOA degradation (Gatto et al., 2015; Lin et al., 2012, 2015). A feasible treatment and remediation strategy is yet in need to address PFOA contamination.

Earlier studies indicated that enzyme catalyzed oxidative humification reactions (ECOHRs) were effective in degrading PFOA under environmentally relevant conditions, and thus potentially feasible for remediation applications (Colosi et al., 2009; Luo et al., 2015). ECOHRs are involved in natural humification processes mediating degradation of lignocellulosic materials as well as polymerization of small humic precursor molecules into humic substances. A number of extracellular enzymes such as peroxidases and phenol oxidases can mediate ECOHRs in soil (Guggenberger, 2005).

Laccases are a group of phenol oxidases that mediate ECOHRs, and have been well studied for their roles in the natural wood delignification process (Woolridge, 2014). Laccases can directly react with substrates containing phenolic or anilinic functional groups to convert them into active intermediates such as radicals and quinones (Du et al., 2013; Piccolo et al., 2000). These active intermediates can further react with recalcitrant organic matters such as lignin, one of the most persistent natural organic materials in the environment, to cause their degradation. Such laccase-mediator systems have been shown capable of degrading persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) (Keum and Li, 2004) and polycyclic aromatic hydrocarbons (PAHs) (Cañas et al., 2007; Johannes and Majcherczyk, 2000). The mediators such as 1-hydorxybenzotriazole (HBT), vanillin, and ferulic acid have been used in these studies because of their high efficiency and low environmental impact (Cañas et al., 2007). These model mediators also contain functionalities that are commonly present in natural organic matter.

Our recent study revealed that 1.00 μmol L^{-1} PFOA in a mineral buffer was degraded about 50% via ECOHRs after 157 days of incubation (Luo et al., 2015). It was proposed that the benzotriazole nitroxyl radical (BTNO) generated from HBT during ECOHRs induced the decarboxylation of perfluorocarboxylic acids (PFCAs) to form perfluoroalkyl radicals, which further reacted with other non-fluorinated free radicals also generated by ECOHRs to form partially fluorinated cross-coupling compounds.

In this study, we systematically evaluated the kinetics of PFOA degradation in laccase-HBT systems with key conditions varied, including PFOA and HBT concentrations and ionic composition, in an attempt to identify factors controlling the reaction rate. It was found in particular that the multivalent ions presented in the solution played a significant role, and the mechanism was elucidated. The results provide a basis to assess the feasibility of ECOHRs in PFOA remediation and approaches to optimize the process for potential application.

2. Material and methods

2.1. Chemicals and reagents

Perfluorooctanoic acid (PFOA), laccase from *Pleurotus Ostreatus* (EC1.10.3.2), 1-hydroxybenzotriazole (HBT), and 2,6-dimethoxyphenol (DMP) were purchased from Sigma-Aldrich (St. Louis, MO). Perfluorocarboxylic acids (PFCAs) with total carbon-chain length from C4-C11 and a surrogate standard perfluoro-n-[^{13}C8]-octanoic acid (M8PFOA) were obtained from Wellington Laboratories (Ontario, Canada) (Supplementary Data Table S1). Cupric/magnesium/manganese sulfates, citric acid, and sodium citrate were from Fisher Scientific (Pittsburgh, PA). All organic solvents were HPLC-grade and also from Fisher Scientific, including acetonitrile, methanol, and dichloromethane.

2.2. PFOA degradation experimental setup

The PFOA degradation experiments were carried out in polypropylene bottles with continuous shake (120 rpm) at 22 °C in an incubator (Innova 42, New Brunswick Scientific). Each reaction bottle contained 100-mL solution with PFOA initial concentration of 1.00 or 100 μmol L^{-1}. The solution was prepared in a mineral buffer, a citric buffer, or a solution containing different metal ions (Cu^{2+}, Mg^{2+}, and Mn^{2+} at 0.1, 1.0, or 10 mmol L^{-1}, respectively, or Fe^{3+} at 0.2 mmol L^{-1}) for comparison. The mineral buffer recipe was derived from a formula that has been used for fungal cultivation (Liu et al., 2013) with the concentration of each component reduced 10 times. The major components of the mineral buffer included $CuSO_4$, $MgSO_4$, and $MnSO_4$. Details for the preparation of each solution were provided in Supplementary Data. The pH values for the mineral buffer and the citric buffer were both 4.5. The metal ion solution was prepared without additional pH buffering, and the determined pH for each metal ion solution was listed in Table S2 (Supplementary Data). Each reactor also contained 0, 20 or 100 μmol L^{-1} HBT and was dosed with 1 U mL^{-1} laccase to initiate ECOHRs. Every six days during the treatment, the reactor was repeatedly dosed with freshly prepared enzyme stock solution to replenish the laccase activity at 1 U mL^{-1}, while at the same time 0, 20 or 100 μmol L^{-1} of HBT was also added to the corresponding treatment. Samples without laccase or HBT and a blank control without addition of both were also prepared and processed at the same time with the same volume of HPLC water and acetonitrile supplemented instead of enzyme and HBT stock solution. An additional experiment was conducted to investigate PFOA degradation via ECOHR in Cu^{2+} solution with the addition of DIPPMPO, a spin trap that can effectively scavenge HBT free radicals. The detail is provided in the Radical Scavenger Experiment in Supplementary Data.

Samples were withdrawn from each reactor at preselected time intervals. For the experiment with initial PFOA nominal concentration of 1.00 μmol L^{-1} (0.414 mg L^{-1}), triplicates of 0.5-mL solution were sampled from each reactor and mixed with 0.5 mL of 0.5-μmol L^{-1} M8PFOA as a surrogate standard. For the experiment with initial PFOA nominal concentration of 100 μmol L^{-1} (41.4 mg L^{-1}), triplicates of 0.1-mL samples were taken, and each was diluted with 0.9 mL HPLC water, from which a 0.1-mL subsample was taken and mixed with 0.5 mL of 0.5-μmol L^{-1} M8PFOA. All mixtures were subjected to solid phase extraction cleanup as reported in our previous study (Luo et al., 2015) (a brief description is provided in Supplementary Data) and then analyzed for PFCAs and HBT concentrations described below. The variation of concentrations caused by solution evaporation and the supplement was adjusted by weighing the reaction solution before and after each supplement event. A 20-μL solution from each reactor was taken every six days for laccase activity assessment using a method reported previously (Park et al., 1999). One unit of laccase activity is defined as the amount of enzyme that causes one unit change in absorbance at 468 nm per minute of a DMP solution at pH 3.8 in a 1 cm light path cuvette (Park et al., 1999) (details are included in Supplementary Data).