



Reductive defluorination of perfluorooctanoic acid by zero-valent iron and zinc: A DFT-based kinetic model



Jens Blotevogel^{a,*}, Robert J. Giraud^b, Thomas Borch^{a,c,d}

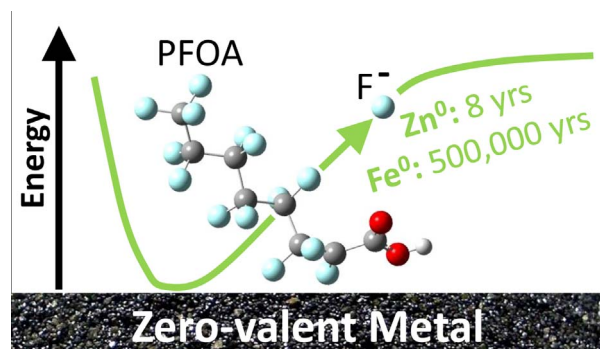
^a Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523, USA

^b The Chemours Company, Wilmington, DE 19899, USA

^c Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA

^d Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO 80523, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

PFOA
PFAS
Reductive defluorination
Zero-valent iron
Permeable reactive barrier

ABSTRACT

Over the past two decades, groundwater contaminated with chlorinated organic compounds has been successfully remediated via reductive dehalogenation by zero-valent iron. While reductive defluorination of the environmentally persistent perfluorooctanoic acid (PFOA) by Fe^0 and Zn^0 is thermodynamically favorable, no successful zero-valent metal applications have been reported yet. Consequently, we developed a combined experimental-theoretical approach based on density functional theory to predict the kinetics of reductive PFOA defluorination as a function of reduction potential. The theoretical model was calibrated with experimental results for the reductive dehalogenation of the structurally similar compound tetrachloroperfluorooctanoic acid to account for the typical non-standard conditions in remedial systems, such as increased pH and metal surface passivation. Our model estimate reveals that the half-lives for the first reductive PFOA defluorination step are ~8 years for Zn^0 and ~500,000 years for Fe^0 at metal-to-water ratios typical for permeable reactive barriers. Therefore, we conclusively document that – in contrast to chlorinated solvents – reductive dehalogenation by zero-valent metals is not a viable remedial approach for PFOA unless suitable catalysts are identified.

1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are ubiquitous

anthropogenic contaminants of extraordinary environmental persistence due to the unique strength of the C–F bond [1–4]. Among them are perfluoroalkyl acids (PFAAs) such as perfluorooctanoic acid (PFOA),

* Corresponding author at: Department of Civil and Environmental Engineering, 1320 Campus Delivery, Colorado State University, Fort Collins, CO 80523-1320, USA.
E-mail address: jens.blotevogel@colostate.edu (J. Blotevogel).

<http://dx.doi.org/10.1016/j.cej.2017.10.131>

Received 29 June 2017; Received in revised form 18 October 2017; Accepted 20 October 2017

Available online 21 October 2017

1385-8947/© 2017 Elsevier B.V. All rights reserved.

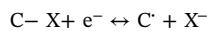
$C_8HF_{15}O_2$), which has been used as a processing aid in the production of polytetrafluoroethylene (PTFE) and other fluoropolymers [3,4], but is also formed during biotransformation of fluorotelomer precursors [5]. U.S. EPA has established a drinking water health advisory at 0.07 $\mu\text{g/L}$ and included it in its updated Contaminant Candidate List 4 (CCL4) on November 17, 2016 [6,7]. Since listing on CCL4 may require future regulation under the Safe Drinking Water Act (SDWA), technologies for remediation of groundwater sources of drinking water warrant evaluation.

Several advanced oxidation processes such as electrochemical treatment [8–10], photo(cata)lysis [11], and heat-activated persulfate [12] have shown promise in degrading PFOA. Reports on successful reductive defluorination, however, are scarce and limited to applications involving the solvated electron as reductant ($E_H^0 = -2.9\text{ V}$) [13–15]. Hori and co-workers [16] observed decomposition of perfluorooctanesulfonate (PFOS) by Fe^0 , but only in subcritical water (350 °C, > 20 MPa). Yet, reductive dehalogenation by zero-valent metals (ZVMs) has been successfully applied to remediate groundwater contaminated with chlorinated volatile organic compounds (CVOCs) for over two decades [17–19]. Zero-valent iron is the most commonly used reductant, transforming chlorinated aliphatics either by dihaloelimination, where two vicinal halogen atoms are released under formation of an additional carbon–carbon bond, or by hydrogenolysis, where a halogen is replaced by hydrogen. While the reductive defluorination of PFOA by Fe^0 ($E_H^0 = -0.44\text{ V}$) [19] and Zn^0 ($E_H^0 = -0.76\text{ V}$) [16] is thermodynamically favorable (Fig. S1), it is expected to be slower than reductive dechlorination reactions because fluorine is missing a low-lying vacant d orbital to accept an electron.

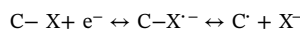
Given the paramount success of ZVMs in driving reductive dehalogenation reactions of CVOCs, it appears reasonable to assume that many researchers have tried to apply this process to PFOA and other PFASs. We therefore interpret the absence of affirmative reports as a failure of ZVMs to achieve reductive defluorination within practical time frames. Nevertheless, documentation of well-executed, but failed treatment approaches is critical to save further resources and guide better solutions. Consequently, the overarching objective of our study is to estimate the kinetics for the reductive defluorination of PFOA by the widely used reductants Fe^0 and Zn^0 . Here, we have developed a theoretical approach based on density functional theory (DFT) to predict the kinetics of reductive dehalogenation as a function of the reduction potential. This free energy relationship is then calibrated using experimental results for the partially chlorinated, structurally related compound 3,5,7,8-tetrachloroperfluorooctanoic acid (TCPFO, $C_8HCl_4F_{11}O_2$) to account for non-standard conditions in remedial systems (e.g., permeable reactive barriers, PRBs), such as increased pH and metal surface passivation [18,20]. By developing this modeling approach, we also address another critical environmental research challenge: the quantification of (degradation) reactions that are too slow to practically measure [21].

2. Theoretical model

To predict dehalogenation kinetics as a function of reductant strength, we used an approach suggested by Savéant [22]. In this approach, the crossing points between potential energy surfaces (PES) for the neutral parent compound and the first radical reduction intermediate along a reaction coordinate are determined. The difference in free energy between PES crossing point and ground state of the neutral parent equals the free energy of activation ($\Delta^\ddagger G$, Fig. 3). This approach assumes that the first one-electron transfer from the reductant to the halogenated species is rate-limiting and thus the only step to be kinetically considered, independent of whether overall (two-electron) dehalogenation occurs via hydrogenolysis or dihaloelimination [23]. However, both a concerted mechanism (where electron transfer and halogen release occur concurrently, and the carbon-halogen bond is the reaction coordinate):



and a stepwise mechanism (where halogen release occurs after electron transfer, and a linearized reaction coordinate ξ is used [24]):



need to be evaluated to determine the more favorable one. The appeal of this model is that it renders cumbersome and costly explicit theoretical modeling of a complex metal surface unnecessary.

All calculations were performed in Gaussian09 at the M06-2X/6-311++G(2d,2p) level of theory, with potential energy minima verified by frequency calculations. Unrestricted methods were used for all open-shell systems. Geometries were optimized without constraints, except for bond lengths and angles along the respective reaction coordinates. The M06-2X functional was chosen due to its excellent performance regarding main-group thermochemistry and kinetics involving radical species [25,26], and as best compromise between accuracy and computational time. This functional, along with the 6-311++G(2d,2p) basis set, has been applied successfully in comparable studies [24,27,28]. The implicit SMD model was used to account for aqueous solvation energies [29]. Bond dissociation energies indicated that the carbon-halogen bonds at C_2 in (linear) PFOA and C_5 in TCPFO would be the most favorable to be broken (Tables S1 and S2), and only C-X dissociations at these positions were further considered to minimize the number of potential energy surfaces to be investigated.

3. Materials and methods

3.1. Batch experiments

To investigate the reactivity of fluorochemicals towards zero-valent metals, triplicate batch experiments in 60-mL wide-mouth screw-cap amber HDPE bottles (VWR) were set up, containing either 10 mg/L PFOA (96% purity, > 98% linear, Sigma Aldrich) or 15 mg/L TCPFO (95%, Synquest Laboratories) in 30 mL degassed and N_2 -purged DI water. Fe^0 (50–70 mesh filings, Fisher Scientific) and Zn^0 (30 mesh granular, certified ACS, Fisher Scientific) were prepared according to Fennelly & Roberts [30] (acid-washing of Fe^0 with 1 M HCl, Zn^0 with 0.4% H_2SO_4 , followed by triple DI water and final acetone rinsing) except for drying under 98:2 $N_2:H_2$ instead of argon atmosphere. Both ZVMs were added to reach a final concentration of 125 g/L, except for TCPFO/zinc batches, where a lower concentration of 25 g/L Zn^0 was used due to fast reduction kinetics. BET analyses revealed specific surface areas (a_s) of 3.71 m^2/g for acid-washed Fe^0 and 0.280 m^2/g for acid-washed Zn^0 . Long-term PFOA batches were vented weekly to release pressure build-up from evolving H_2 gas. Metal preparation, batch setup, venting and storage ($23 \pm 2^\circ\text{C}$) occurred in an anoxic chamber holding a 98:2 $N_2:H_2$ atmosphere.

TCPFO batches were sampled within the anoxic chamber. PFOA batches were removed from the chamber and sacrificed at the time of sampling. For organofluorine analysis, 2-mL aqueous samples were filled into 2-mL borosilicate glass LC headspace vials. For ion chromatography analysis, 300- μL aqueous samples were filled into 0.5-mL PolyVials (Dionex). For ion selective electrode analysis, 15-mL aqueous samples were filled into 40-mL borosilicate glass vials and adjusted with total ionic strength adjustment buffer (TISAB, Cole-Parmer) to pH 5.8 according to manufacturer's specifications. For PFOA, the solid phases (i.e., interior walls of the batch containers, plus zero-valent metals when present) were extracted by adding 10 mL methanol followed by one minute of manual agitation and ten minutes on a vortexer.

3.2. Chemical analyses

Organofluorine compounds were analyzed with an Agilent 1100 Series liquid chromatograph equipped with a $4.6 \times 150\text{ mm}$, 5 μm ZORBAX Eclipse XDB-C18 column (Agilent) in combination with an

Download English Version:

<https://daneshyari.com/en/article/6580819>

Download Persian Version:

<https://daneshyari.com/article/6580819>

[Daneshyari.com](https://daneshyari.com)