Saerom Park

Lab-scale Exploration of Abiotic Transformation Approaches for Groundwater Remediation for Per-and Polyfluoroalkyl Acids

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Abstract

Per- and polyfluoroalkyl acids (PFAAs), a group of per- and polyfluoroalkyl substances (PFASs), have been extensively used in relatively large amount since the 1950s for industrial and consumer applications such as surfactants, coatings, paper packing products, and fire-fighting foams (e.g., aqueous film-forming foams (AFFFs)) due to their unique surfactant property and extremely chemically and thermally stable nature. Of the known PFAAs, long chain perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have received increasing attention in recent years due to their global distribution, environmental persistence, biological recalcitrance, bioaccumulative properties, and potential toxicities. Recently, other PFAAs such as 6:2 fluorotelomer sulfonate (6:2 FTSA) and perfluorohexane sulfonate (PFHxS) were also added to the list of USEPA Unregulated Contaminant Monitoring Regulation (UCMR3).

Research presented here focused on exploring at the lab-scale 4 technologies with potential for use in-situ remediation of groundwater contaminated with PFAAs: (1) the abiotic oxidation of PFOA, 6:2 FTSA, and PFOS using heat-activated persulfate (PS, 4.2~84 mM) at 20~60°C; (2) nanosized zero valent iron coated with palladium (Pd^0/nFe^0 NPs) to transform PFOS, which was not transformed with PS; (3) vitamin B12 (VB12) with nanosized zero valent zinc (nZn^0) to defluorinate both branched (br-) and linear (L-) PFOS and PFHxS isomers; and (4) permanganate (PM)-base technologies to transform PFOS in buffered and unbuffered solutions at 65°C. In all studies, PFAA removal (or transformation) was quantified by comparing the combined PFAA mass in aqueous phase and extracts if solid particles were present to the initial PFAA mass measured in the applied PFAA solutions.

PFOA was successfully oxidized using heat-activated PS sequentially removing CF_2 groups to shorter chain perfluoroalkyl carboxylic acids (PFCAs). 6:2 FTSA was also oxidized first breaking the ethyl linkage and CF_2–CH_2 bond generating PFCAs with subsequent CF_2 removal like PFOA. No PFOS removal was observed even at 90°C and using higher PS concentrations (84 mM). In the Pd^0/nFe^0 NPs systems, ~26% of PFOS removal was observed in 6 d at 45°C and initial pH of 3.4 whereas at 21 d, PFOS removal was reduced to <~5 %. Furthermore, generation of F^- and SO_4^{2-} as products of PFOS transformation was not observed indicating that PFOS was not transformed. X-ray diffraction analysis (XRD) indicated that apparent PFOS removal with Pd^0/nFe^0 NPs was due to strong adsorption of PFOS (not extractable) onto $Fe(OH)_3$ formed via nFe^0 corrosion. Subsequently, PFOS was released through the conversion of $Fe(OH)_3$ to less sorptive FeO(OH) via Fe(II) catalyzed transformation. In the process of exploring the reasons for apparent PFOS removal with Pd^0/nFe^0 NPs, PFOS as well as other PFAAs were found to form complexes with Fe(II/III) ions. Complexed PFOS was not detected for quantification by mass spectrometry (MS). In the VB12 with nZn^0 systems, br- isomers of PFOS and PFHxS were successfully defluorinated. However, L- isomers were not altered; thus, limiting its usefulness for groundwater remediation given the dominance of L-isomer. As organic intermediates/products of br-PFOS and br-PFHxS defluorination, C8- and C7- based polyfluorinated sulfonates and C6- and C5- based polyfluorinated sulfonates were identified, respectively. Lastly, no PFOS removal was observed using PM-based technologies even with the use of Ru(III), $NaHSO_3$, Fe(II), 2,2'-azino-bis(3-ethyl benzothiazoline)-6-sulfonate (ABTS), microsized zero valent metals: mMg^0 and mFe^0 to catalyze the reaction.

None of the technologies explored were successful in transforming both L- and br- per/polyfluoroalkyl caboxylates and sulfonates that co-occur at most sites. However, this study has contributed to insight into the intermediates/products and defluorination pathways of br-PFOS and PFHxS which can be used to design other remediation strategies and to study fate and transport of them in environment mediums.