

Removal and Destruction of Perfluoro- and Polyfluoroalkyl Substances (PFAS) from Contaminated Groundwater through Application of Advanced Reductive Processes (ARPs)

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Background/Objectives. One of the greatest challenges facing remediation scientists and engineers is the cleanup of sites contaminated by perfluoro- and polyfluoro-alkyl substances (PFAS). Compared to other legacy pollutants like halogenated solvents, fuel hydrocarbons, and nitro explosives, PFASs are much more recalcitrant, structurally diverse, non-volatile, and mobile. As a result, they are very challenging to monitor, treat, and contain onsite. Natural attenuation via biological and abiotic processes is not a viable option. As a result, many efforts are underway to develop advanced treatment technologies for PFAS. PFAS removal from groundwater can be accomplished using activated carbon adsorption, ion exchange, and high pressure membrane separation (i.e., NF/RO). While these processes are successful, to a degree, they only serve to transfer the PFAS from groundwater to another (more concentrated) phase. To date, strategies for PFAS destruction have focused on advanced oxidation processes (AOPs) generating strong oxidizing radicals (hydroxyl and sulfate radicals), but these are largely ineffective, especially for perfluoroalkyl sulfonic acids (e.g., PFOS). Here, we describe recent efforts to apply advanced reductive processes (ARPs) that generate a strong reducing species (hydrated electrons, e_{aq}^- ; $E_H = -2.9$ V).

Approach/Activities. Hydrated electrons are produced using commercial UV reactor systems together with the photosensitizer sulfite (i.e., UV-sulfite treatment), a low cost bulk chemical already used by water and food industries. Direct treatment of contaminated groundwater and treatment of concentrate streams (e.g., NF reject) will be discussed. High resolution mass spectrometry analysis is applied to monitor transformation of a wide diversity of PFAS structures (>1000 structures in the target screening list) during UV-sulfite treatment. Treatment by UV-sulfite will be compared to UV-persulfate treatment (produces oxidizing sulfate and hydroxyl radicals), and the strengths and limitations of the two processes will be discussed.

Results/Lessons Learned. Work by our team and others shows that a wide range of PFAS structures, including both perfluoroalkyl carboxylates and perfluoroalkyl sulfonates, can be degraded and defluorinated by UV-sulfite processes. Degradation of a wide range of perfluoroalkyl acid precursors (e.g., sulfonamides) are also demonstrated. Results provide information on structure-reactivity trends and the influence of non-target groundwater constituents (e.g., hardness, alkalinity, nitrate). Overall, UV-sulfite is able to successfully treat a wider range of PFAS structures compared to UV-persulfate. Comparisons based upon both UV fluence and chemical additives will be discussed, and opportunities for hybrid processes (e.g., ion exchange with concentrate management by UV-sulfite) will also be discussed.