

Diamond Materials for Solvated Electron Chemistry
Potential Payoff: Remediation of AFFF PFAS Contamination from Water

PI: Bradford Pate, code 6178

Poly- and per-fluoroalkyl substances (PFAS) are synthetic chemicals found in clothing, furniture, cookware, food packaging, cosmetics and aqueous film forming foam (AFFF or “firefighting foam”). In 1966 NRL patented the use of PFAS as a surfactant in AFFF.[1] PFAS are now known to be highly persistent, bioaccumulative, toxic, and have infiltrated numerous water sources in the United States. [2] Perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) are PFAS with an EPA health advisory level (HAL) of 70 parts per trillion in ground water (issued in June 2016). The 2016 health advisory reduced the advisory threshold for PFOS and PFOA contamination in municipal water supplies by an order of magnitude. NAVFAC has determined that the EPA HAL for PFASs have been exceeded at several Navy installations including NASJRB Willow Grove, NAS Warminster, NAS Brunswick, NAS Corpus Christi, and NAS Jacksonville. In August 2016, the U.S. Navy was sued for the first time over contamination exceeding the EPA advisory for PFOS and PFOA in ground water.[3] Today’s focus on remediation are the so-called C8 class (eight carbon chain) of PFAS that specifically include PFOS and PFOA. However, a comprehensive remediation process that is effective not only for C8, but also shorter chain PFAS is called for.

Contrary to naturally occurring fluorinated compounds that typically contain a single fluorine atom, anthropogenic PFAS contain carbon backbones that are nearly saturated with fluorine. As a consequence these molecules are extremely recalcitrant, with no known biodegradation or abiotic degradation pathway, and persist on a decades time scale in the environment. [4] This coupled with aqueous solubility imparted by their functional head groups and weak sorption properties has resulted in far reaching, rapid contamination of water sources. [2] While the weak sorption properties of PFOA and PFOS to organics in the environment allow them to travel to remote regions of the Atlantic, Pacific and Arctic oceans, their interaction with proteins enable them to bioaccumulate resulting in high levels of PFAS being detected in animals and humans. PFAS exposure is a concern as these substances have been linked to cancer, obesity, high cholesterol, immune suppression and endocrine disruption. [5,6]

Standard wastewater treatment methods are not only ineffective for the removal of PFOS and PFOA, but also serve as a source, since labile precursors biodegrade into PFOS and PFOA. [7,8] Recent reports of fluorotelomer-based polymers (FTPs) have also implied these compounds may undermine efforts to reduce PFOAs for years to come by degradation into perfluorocarboxylic acids. [9] Although a number of treatment technologies have been demonstrated for PFOA and PFOS removal, such as reverse osmosis, nanofiltration, and activated carbon, the results are varied and include hazardous waste disposal of concentrated PFAS and/or economical constraints. [10] In this regard, concentrated PFAS disposal is not a trivial process and must include a sustainable approach that does not simply transfer PFAS waste from one hazardous form to another. Pyrolytic destruction though attractive and currently in practice, must address the release of fluorinated volatiles. Since the C-C bond is weaker than the C-F bond, the carbon chain is more susceptible to cleavage during incineration resulting in short chained fluorocarbons that may contribute to atmospheric contamination and potentially greater exposure to humans. Similarly advanced oxidation processes, which use chemicals, catalysts and light to oxidize chemicals with hydroxyl radicals, are prone to generating short chained PFAS intermediates that are more volatile along with deadly fluorine gas as a by product. [11]

Only strongly reductive processes have demonstrated the ability to separate fluorine atoms from the carbon chains of PFC, due to the extreme reduction potential (E) required to break the carbon-fluorine bond, $E < -2.7 \text{ V}$ vs. standard hydrogen electrode. And, in water, defluorination of PFAS is

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recognized as being accessible only by aqueous electrons. [10] Our approach, direct injection of electrons into solution from negative electron affinity diamond, is a chemical free source of highly reductive aqueous electrons that would consequently provide a critical technology that is currently missing in the treatment and waste disposal of PFAS in water. An encounter of PFAS with aqueous electrons generates only fluoride ions and hydrocarbons (free hydrogen in solution replaces the fluorine), each of which can be removed by well-established wastewater treatment technologies. For fluoride removal from municipal water supplies, the EPA finds the most cost effective process often is the use of activated alumina for adsorption of fluoride via ligand exchange, with periodic regeneration of the activated alumina. [12] This is a well established technique that is widely used in the U.S. where the amount of naturally occurring fluoride in water exceed the recommended level of 700 ppb (factor of 10,000 above the health advisory limit for PFAS). The captured fluoride, is recovered periodically in a regenerative process that re-activates the alumina and converts the adsorbed fluorine ions to disposable metal salts (eg. CaF). There are numerous established adsorption or oxidation processes for removal of the remnant hydrocarbons from water.

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