LLNL-TR-813911

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Survey of PFAS Treatment Technologies

R. Lenear, A. Chang

August 25, 2020

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Survey of PFAS Treatment Technologies

Raina Lenear 7/2/2020

Per- and polyfluoroalkyl substances (PFAS) are a group of manufactured chemicals that have caught the attention of many governmental agencies and researchers. These chemicals are highly stable and possess hydrophobic properties that lead to the widespread use of PFAS in aqueous film forming foams, and household products such as carpets, paper and non-stick cookware (Prevedouros et al., 2006). Regulatory and health advisories have focused determining a lifetime drinking water health advisory of 70 ng/L for PFOA and PFOS (USEPA, 2016). Other PFASs may be present in the environment, along with PFOA and PFOS, due to product manufacturing processes (Prevedouros et al., 2006). A variety of proprietary AFFF formulations were manufactured and sold during different timeframes, thereby complicating the signature and distribution of PFASs in groundwater beneath former firefighting training areas (McGuire et al., 2014). PFOA and PFOS are stable chemicals that persistent in the environment and are difficult to remediate. The understanding of the physicochemical properties and fate and transport of PFASs in groundwater is growing but is still limited (USEPA, 2012). Many traditional approaches such as coagulation and conventional water treatment are ineffective in treating PFOA and PFOS. Selecting the most appropriate remedial strategy for PFOA and PFOS is therefore challenging. In this survey findings from the literature on PFASs removal using various technologies were compiled.

Granular Activated Carbon and Anion Exchange

Multiple PFASs were successfully removed using Granular Activated Carbon (GAC) and Anion Exchange (AE) columns. The AE and GAC adsorbent columns successfully removed the 14 PFASs in this study with an average removal efficiency 66% for the AE column and 62% for the GAC. Neither the AE nor GAC columns showed evidence of PFSA desorption during the testing, however, desorption may still occur for the short-chained PFAS. The adsorption of the 14 PFASs by the AE and GAC columns was characterized by an increase in removal capacity after ~60 and ~50 days, respectively. This increase may be due to a transition of the removal mechanism from

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

being a function of open sites on the absorbents (Phase 1) to agglomeration of PFASs on the absorbent surface (Phase 2) which provides a more hydrophobic site for attachment of PFAS molecules. In addition, dissolved organic carbon loading may facilitate the agglomeration process, although the DOC removal efficiency did not correlate to PFAS removal efficiency for the AE or GAC column. GAC has been found to offer more economical performance compared to other removal techniques such as reverse osmosis and some advanced oxidation processes (Bartell et al., 2010, Deng et al., 2014). GAC consistently removes PFOS with an efficiency of more than 90% (Ochoa-Herrera et al., 2008). The sorption kinetics are faster for longer-chained PFASs and smaller-diameter GAC particles, therefore, GAC that is optimized for PFOS removal may not optimally remove other PFASs (Rayne and Forest, 2009). During recent discussions on PFAS treatment, concerns were raised regarding the potential for smaller chain PFASs (four or six carbons) to break through the GAC media within shorter timeframes than their longer chain equivalents (Deeb, 2015). Such compounds have yet to be evaluated for their impact on human health and the environment, and may be subject to future regulation pending such evaluations.

Thermal Destruction

Thermal destruction is commonly used for used granular activated carbon and other waste byproducts of water treatment. Despite the highly oxidized nature of the PFOA and PFOS, PFASs display a relatively high thermal reactivity (Lee et al., 2012). The temperature used for thermal incineration of PFASs is usually greater than 1000 °C (Lee et al., 2013); however, in laboratory studies more than 99% PFOS is degraded at 600 °C. In case of long-chain PFAS salts, pyrolysis yields products such as the perfluoroalkylacetyl fluorides and acids. It was found that the required degradation temperature increased with increasing perfluoroalkyl chain lengths (Rayne and Forest, 2009).

Novel adsorbents with increased adsorption performance and the potential for decreased costs are starting to appear as a topic of laboratory research. Some new materials such as cross-linked chitosan beads of greater adsorption capacity for PFOS at pH 3 have been reported (Zhang et al., 2011). When the pH of the tested solution was adjusted to 3.0, over 99.4% of the amino groups of the chitosan beads were protonated, and thus the negatively charged PFOS was easily adsorbed, resulting in its increased removal. The final sorption capacity of optimized chitosan biosorbent was reported at up to 5.5 mmol/g for PFOS at the equilibrium concentration of 0.33 mmol/L, which is much higher than conventional absorbents.

Filtration

A variety of diverse types of membranes can be implemented for PFAS treatment including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis membranes. Nanofiltration and reverse osmosis membranes are theoretically more applicable for PFAS filtration due to the desirable pore sizes. First studies on filtration with RO showed over 99% rejections of PFOS compounds (Tang et al., 2006). Nanofiltration membranes in combination with reverse osmosis had a high success rate when tested on a feed of 10 parts per million PFOS over 4 days (Tang et al., 2007). The rejection of PFOS for RO membranes was typically higher than 99%, while the removal for nanofiltration membranes ranged from 90 to 99% due to the slow penetration of molecules through smaller pores on the surface of the nanomembrane. The removal of PFOS was generally greater with higher pressure for a given type of membrane.

Sonochemical destruction

Sonochemistry is the use of acoustic fields to generate chemical reactions in a solution. Sound waves collapse the bubbles in the solution, resulting in high vapor temperatures and decomposition of PFASs at the bubble-water interface (Hao et al., 2014). Typical ultrasound frequencies applied during the sonochemical treatment of PFASs range from 20 to 1000 kHz. The half-lives of PFOA and PFOS have been reported at 43 and 22 min, respectively, when treated under an argon atmosphere and 102 and 45 min under an air atmosphere (Rayne and Forest, 2009) with the concurrent production of shorter-chain PFASs. The sonochemical reactions were performed with PFOS and PFOA concentrations ranging from 20 nM to 200 µM and with irradiation of 354 kHz. The decrease in concentration of PFOS and PFOA ranged from 39% to 44%, respectively.

The primary surfactants and PFOS were sonochemically degraded over a range of dilutions, 65 µg/L to 13,100 µg/L of PFOS. Sonochemical methods can be used on large quantities of AFFF at a larger scale to treat large stockpiles of toxic fire-fighting chemicals (McGuire et al., 2014). This innovative approach will be applied to unused inventory of AFFF products stored at Air Force sites to aid in the development of a system to produce the required high incineration temperatures and desired concentration of active oxidizing radicals, while consuming the least amount of energy.

Electrochemical Destruction using Boron-Doped Diamonds

This treatment is based on the oxidative destruction of PFOS using boron-doped diamond film electrodes. Experiments measuring oxidation rates of PFOS were performed over a range in current densities and temperatures using a rotating disk electrode reactor and a parallel plate flow-through reactor. The oxidation of PFOS yields sulfate, fluoride, carbon dioxide, and trace levels of trifluoroacetic acid. Short chains are made, but vary in different waters (Carter et al., 2008). Precursor transformation is a crucial knowledge gap for treatment using any technology. Researchers at CDM Smith have studied PFAS remediation with boron-doped diamond electrodes deposited using.

Photocatalysis

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. Heterogeneous photocatalysis is an effective technology for PFAS degradation. Photocatalysis performs well in acidic medium and increased with temperature. Dissolved organic matter reduces photocatalytic performance in wastewater. In2O3 nanoplates degrade 100% PFAS under UV light (Xu, B. et al., 2017). Titanium Oxide (TiO_2) is a feasible photocatalyst choice due to its chemical and physical stability, availability, low cost, nontoxicity and the ability to degrade a diverse range of chemicals from water (Xu et al., 2014). It has been reported that perfluorocarboxylic acids (PFCA) with perfluorinated carbon chain could be decomposed by more than 85% within 420 min treatment

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

by TiO_2 photocatalysis irradiated with a 16 W low-pressure mercury UV-lamp (Panchangam et al., 2009). TiO_2 can be modified with other elements or compounds to ultimately improve the degradation efficiency. When TiO_2 is used as the catalyst for the degradation of PFOA, the efficiency is increased at $pH < 3.0$ due to the presence of an acidic solution. This suggests that TiO_2 at low pH has better photocatalytic ability.

Sources

Bartell, S. M., Calafat, A. M., Lyu, C., Kato, K., Ryan, P. B., & Steenland, K. (2010). Rate of decline in serum PFOA concentrations after granular activated carbon filtration at two public water systems in Ohio and West Virginia. *Environmental health perspectives*, *118*(2), 222-228.

Carter, K. E., & Farrell, J. (2008). Oxidative destruction of perfluorooctane sulfonate using boron-doped diamond film electrodes. *Environmental science & technology*, *42*(16), 6111-6115.

Contaminants, E., & Sulfonate, P. (2012). *and Perfluorooctanoic Acid (PFOA)*. EPA 505-F-14-001.

Deeb, R. (2015, March). H2O Talk: State-of-the-Practice on Addressing PFC (Perfluoroalkyl Compounds) Impacts. In 2015 NGWA Groundwater Summit. Ngwa.

Deng, S., Nie, Y., Du, Z., Huang, Q., Meng, P., Wang, B., ... & Yu, G. (2015). Enhanced adsorption of perfluorooctane sulfonate and perfluorooctanoate by bamboo-derived granular activated carbon. *Journal of hazardous materials*, *282*, 150-157.

EPA, U. (2016). *Fact Sheet PFOA & PFOS drinking water health advisories*. EPA 800-F-16-003.

Hao, F., Guo, W., Wang, A., Leng, Y., & Li, H. (2014). Intensification of sonochemical degradation of ammonium perfluorooctanoate by persulfate oxidant. *Ultrasonics sonochemistry*, *21*(2), 554-558.

Kucharzyk, K. H., Darlington, R., Benotti, M., Deeb, R., & Hawley, E. (2017). Novel treatment technologies for PFAS compounds: A critical review. *Journal of environmental management*, *204*, 757-764.

Lee, Y. C., Lo, S. L., Kuo, J., & Lin, Y. L. (2012). Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40 C. *Chemical engineering journal*, *198*, 27-32.

Lee, Y. C., Lo, S. L., Kuo, J., & Huang, C. P. (2013). Promoted degradation of perfluorooctanic acid by persulfate when adding activated carbon. *Journal of Hazardous Materials*, *261*, 463-469.

McGuire, M. E., Schaefer, C., Richards, T., Backe, W. J., Field, J. A., Houtz, E., ... & Higgins, C. P. (2014). Evidence of remediation-induced alteration of subsurface poly-and perfluoroalkyl substance distribution at a former firefighter training area. *Environmental science & technology*, *48*(12), 6644-6652.

Ochoa-Herrera, V., Sierra-Alvarez, R., Somogyi, A., Jacobsen, N. E., Wysocki, V. H., & Field, J. A. (2008). Reductive defluorination of perfluorooctane sulfonate. Environmental Science & Technology, 42(9), 3260-3264.

Panchangam, S. C., Lin, A. Y. C., Shaik, K. L., & Lin, C. F. (2009). Decomposition of perfluorocarboxylic acids (PFCAs) by heterogeneous photocatalysis in acidic aqueous medium. *Chemosphere*, *77*(2), 242-248.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Prevedouros, K., Cousins, I. T., Buck, R. C., & Korzeniowski, S. H. (2006). Sources, fate and transport of perfluorocarboxylates. *Environmental science & technology*, *40*(1), 32-44.

Rayne, S., & Forest, K. (2009). Perfluoroalkyl sulfonic and carboxylic acids: a critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. *Journal of Environmental Science and Health Part A*, *44*(12), 1145-1199.

Tang, C. Y., Fu, Q. S., Robertson, A. P., Criddle, C. S., & Leckie, J. O. (2006). Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater. *Environmental science & technology*, *40*(23), 7343-7349.

Tang, C. Y., Fu, Q. S., Criddle, C. S., & Leckie, J. O. (2007). Effect of flux (transmembrane pressure) and membrane properties on fouling and rejection of reverse osmosis and nanofiltration membranes treating perfluorooctane sulfonate containing wastewater. *Environmental science & technology*, *41*(6), 2008-2014.

Xu, B., Ahmed, M. B., Zhou, J. L., Altaee, A., Wu, M., & Xu, G. (2017). Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanism, kinetics and controlling factors. *Chemosphere*, *189*

Zhang, Q., Deng, S., Yu, G., & Huang, J. (2011). Removal of perfluorooctane sulfonate from aqueous solution by crosslinked chitosan beads: sorption kinetics and uptake mechanism. *Bioresource technology*, *102*(3), 2265-2271.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.