

Method of improving interfacial removal of short-chain PFAS

Abstract

Tetra-alkyl ammonium compounds were found to enable high efficiency removal of short- and ultrashort-chain PFAS compounds in synthetic water samples. Using an ECo-PRe Beta plasma reactor (DMAX Plasma, LLC), we identified a family of tetra-alkyl ammonium additives which improve efficiency of PFBS, PFBA, and PFPA destructive removal. Additives include tetrabutyl ammonium hydroxide (TBAOH), tetrahexyl ammonium hydroxide (THAOH), tetraoctyl ammonium hydroxide (TOAOH). The use of these additives yields equivalent or higher removal efficiencies compared to CTAB/OTAB compounds. We observed electrical energy per order efficiencies near 30 kWh/m³ for both PFBS and PFBA removal, and near 400 kWh/m³ for PFPA removal.

Introduction

Methods that remove PFAS from aqueous matrices often rely on the interfacial properties of the surfactant-like PFAS molecules. While some of these methods work effectively for long-chain PFAS, they are inherently less efficient for short-chain PFAS molecules which exhibit lower interfacial activity. Both destructive and non-destructive technologies might benefit from bringing the efficiency of short-chain PFAS removal on par with long-chain. It has been demonstrated that the removal efficiency of short-chain PFAS compounds can be improved by the addition of CTAB to the aqueous matrix (plasma^{1,2}, foam fractionation³). This work demonstrates the utility of tetra-alkyl ammonium additives for increasing the interfacial activity of short-chain PFAS compounds, specifically PFBS and PFBA, and improving their removal efficiency in a plasma treatment system. Tetra-alkyl ammonium compounds were investigated as additives for this process as they were previously found to improve dynamic surfactancy of long-chain PFAS compounds.^{4,5}

Results

PFBA and PFBS were added to deionized water at a target concentration of 100ppb and was treated for 4 hours in an ECo-PRe Plasma Reactor from DMAX Plasma, LLC⁶ (further details are provided in experimental methods). Figure 1 shows the concentrations of PFBS and PFBA, with and without the use of a tetra-alkyl ammonium additive. Without the use of any additives, the concentration of PFBS decreases by less than 50% in 4 hours, while PFBA concentration is unaffected by the plasma treatment process. When tetra-hexyl ammonium hydroxide (THAOH) is added to the water matrix and dosed periodically throughout the treatment process, the removal rates for PFBS and PFBA are significantly higher. From these data, in the presence of THAOH, we calculate the electrical energy per order removal efficiency to be 32 kWh/m³ and 34 kWh/m³ for PFBA and PFBS, respectively.

Figure 2 shows concentrations of four target byproducts (PFPA, 2333-TFPA, 2233-TFPA, and TFA) measured during treatment of PFBS- and PFBA-containing water in the presence of THAOH additive. The detection of these ultrashort-chain PFAS supports the hypothesis that PFBS and PFBA are being

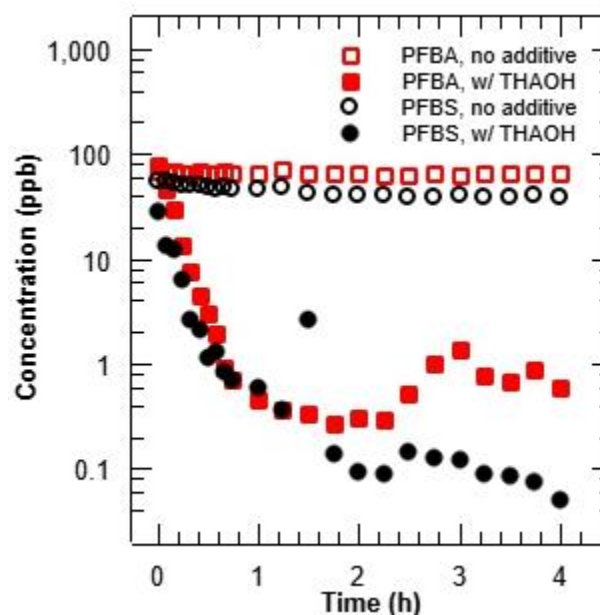


Figure 1. PFBA and PFBS concentrations during water treatment in ECo-PRe Plasma reactor (DMAX Plasma, LLC).

These results are based on laboratory experiments and should not be taken to imply 3M advocacy, approval, or certification for use of these treatments in PFAS remediation. Further processing of a waste stream may be required prior to re-introduction into the environment.

broken down in this process. In the case of PFPA, concentration was observed to increase for the first 20 minutes of treatment, and then decrease. This trend indicates that PFPA may also be degraded in this process and that these tetra-alkyl ammonium additives (THAOH) further improve the breakdown of even ultra-short chain PFAS. From, these data, the electrical energy per order for PFPA removal in the presence of THAOH is 417 kWh/m³. A complete mass balance is out of scope for this work.

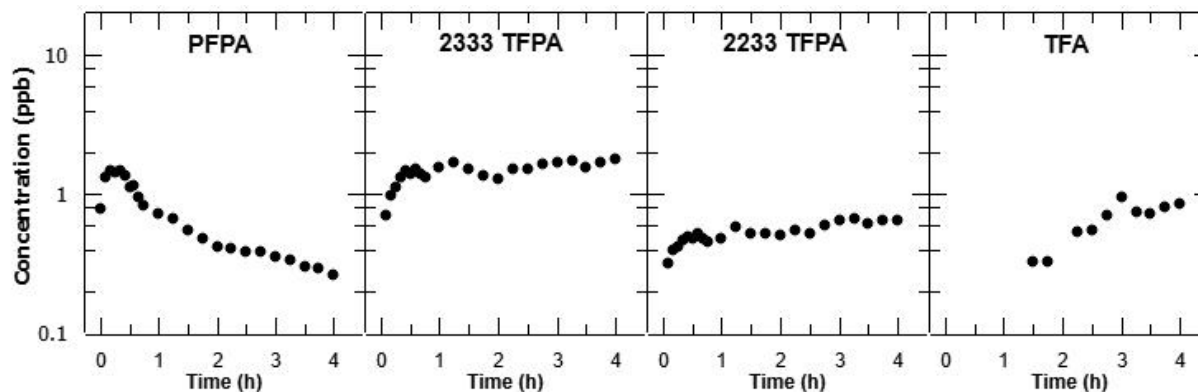


Figure 2. Concentrations of select target analytes measured during treatment of PFBA and PFBS containing water in the presence of THAOH.

Experimental methods

Equipment. A laboratory scale electrical discharge plasma reactor designed for treatment of PFAS containing water was purchased from DMAX Plasma (Enhanced Plasma Contact System “ECo-Pre” Beta Reactor). The system consists of a NEMA enclosure housing a 5.8 gallon treatment tank, a plasma generating network and power supply, and gas and liquid handling equipment. The treatment tank is constructed with a 12”W x 12”D x 18”H HDPE body and thick acrylic lid compressed against a rubber O-ring to form an airtight seal. Baffles within the reactor divide it into 3 chambers, creating a torturous path for water to flow. Water level in the treatment zone is ~13”. Water is circulated through the treatment tank and external cooling loop by a mechanical pump. Pentair Aquatic Ecosystem Sweetwater Model # AS15S diffusers rests on the floor of each chamber, which are continuously supplied with Ar gas, generating bubbles. A stainless steel sawtooth electrode is suspended ¾” above the water surface in each chamber and a stainless steel ground mesh sits approximately 1” below the water’s surface. The power supply and plasma generating network supplies high-voltage pulsed power to the sawtooth electrode. A valved port on the water recirculation line allows for sample collection and additive dosing.

Water Composition. Deionized laboratory water was pumped into the reactor treatment tank. PFAS compounds (PFBA, PFBS) were added to reach a target concentration of 100 ppb. Conductivity was adjusted to 300 uS/cm with NaCl. Water was circulated through the reactor for 30 minutes to ensure thorough mixing. Simultaneously, Ar gas was supplied through the diffusers to purge the treatment tank headspace and de-gas the water. Dissolved oxygen in the water, measured by an EcoSense-ODO200, was purged to less than 0.5 mg/L prior to treatment.

Additive Dosing. Prior to treatment, additives were introduced to the treatment tank at 0.134 mM and the water was circulated for 30 minutes to ensure thorough mixing. Throughout treatment, additives were dosed into the system through the sample port at 0.074 mM every 15 minutes.

Treatment. Power was applied at -25kV, 40Hz to the sawtooth electrodes, generating a pulsed plasma discharge across most of the water’s surface. Ar gas was supplied to the diffusers at a rate of 10.0 lpm throughout treatment, maintaining positive headspace pressure of the treatment tank between 770-870 Torr. The water was circulated through the reactor and cooling loop at a rate of 0.15 lpm to maintain a temperature between 20-45°C. 22.0 mL of water was collected in HDPE bottles every 5 minutes for the first

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45 minutes and every 15 minutes for the rest of the treatment time. Immediately following collection, sample pH and conductivity were measured to ensure constant conditions (~pH 6-9, ~300uS/cm).

Analysis. All test samples and quality control samples were analyzed for the target analytes using high performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS). This is a performance-based method applied to the quantitative analysis of perfluorinated alkyl acids (PFAAs), such as perfluorosulfonic acids and perfluorocarboxylic acids. Test samples were collected in high-density polyethylene bottles and sent to the testing laboratory for preparation and analysis. Samples were diluted with a methanolic solution fortified with stable isotope internal standards to achieve the required test matrix and to quantify target analytes within the calibration range of 0 to 50 ng/L. Quality control samples, including check calibrations, procedural blanks, and laboratory control spike samples, were routinely prepared and analyzed alongside the test samples to verify accuracy and precision.

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