Task ID**:** 425.018

Task Title**:** Destruction of Perfluoroalkyl Surfactants in Semiconductor Process Waters Using Boron Doped Diamond Film Electrodes.

Deliverable**:** Report on the susceptibility of PFAS oxidation and reduction products to biodegradation under conditions relevant to municipal wastewater treatment plants.

Summary Abstract:

PFOS and other perfluorinated alkyl surfactants (PFAS) are widely used in semiconductor manufacturing. Recent studies have detected PFOS in human blood and wildlife tissue samples collected from around the globe. Regulatory agencies in the United States and Europe have initiated studies to quantify the use of PFAS, assess their potential risks, and consider regulations banning or restricting their use.

Much of the PFOS used in semiconductor fabrication is disposed of in solvent-based wastes by incineration. However, there is no effective treatment for the removal of PFOS or any other PFAS compounds from wastewater streams. The carbon-fluorine bonds in fluorinated organics are very stable and have slow reaction rates with the hydroxyl radicals produced in conventional advanced oxidation processes. Membrane methods and ion exchange are expensive and merely concentrate the aqueous compounds which then require disposal. Additionally, perfluorinated surfactants are not biodegradable in municipal wastewater treatment plants.

This research task considers the application of electrochemical treatment for removing PFOS and related perfluoroalkyl surfactants from semiconductor effluents. The aim of the work presented here is to characterize the fate of the incomplete destruction products from electrochemical treatment in conventional biological wastewater treatment systems.

Technical Results and Data:

Electrolysis experiments performed in both parallel plate, flow-through boron-doped diamond (BDD) electrode reactors and in batch reactors using a rotating disk BDD electrode indicated that PFOS can be rapidly removed from water.

Experiments were set up to evaluate the impact of electrochemical treatment on the microbial toxicity of PFOS and on the susceptibility of PFOS to microbial degradation. Bioassays were designed to simulate typical conditions in municipal wastewater treatment plants. Solutions of PFOS (0.52 mM, pH 5.5) were subjected to electrolysis in the batch reactor at a current of 10 mA for time periods ranging from 0 to 24 hours. An exogenous electrolyte was not added to the PFOS solution. The batch reactor had an anode surface area of 1 cm^2 and a solution volume of 350 ml, yielding a surface area to solution volume ratio of 2.86 x 10^{-3} cm^2/ml. Electrochemical treatment resulted in a

gradual decrease in the concentration of total organic carbon (TOC), resulting in 80% removal after 24 hours (Fig. 1). The concentration of PFOS in solution also decreased with electrolysis time, albeit at a slower rate compared to the TOC. The decrease in PFOS content was accompanied by release of fluoride ion (results not shown) which accounted for approximately 7 moles or fluoride per mole of PFOS removed. Figure 2 shows the F-NMR spectra of untreated PFOS and PFOS electrolyzed for 18 hours. The spectrum of treated PFOS only shows a new peak with a shift of approximately -122 ppm that corresponds to the fluoride ion.

Electrochemical treatment was found to increase the microbial toxicity of PFOS (Fig. 3A). The untreated PFOS solution (0.42 mM) caused moderate inhibition of the metabolic activity of the methanogenic inoculum (30% reduction compared to the uninhibited control). In contrast, exposure to the electrolyzed PFOS solutions led to

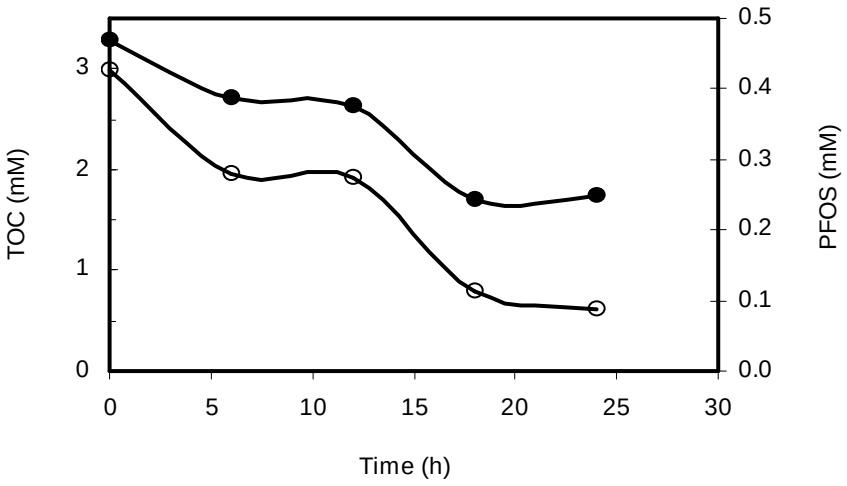

Fig. 1. Concentration of PFOS (●) and total organic carbon or TOC (○) as a function of time in an electrolysis experiment conducted in a BDD batch reactor operated at a current of 10 mA.

decreases in the microbial activity ranging from 58 to 70%. Additional experiments performed with the solution subjected to electrolysis for 24 hours (Fig. 3B) indicated that the toxicity decreased rapidly with sample dilution. The microbial inhibition of a solution diluted two-fold was only 31%. It is likely that at least part of the toxicity was due to the relatively high concentrations of fluoride released by electrochemical attack of PFOS (up to 44 mg/l after 24 hours of treatment). Fluoride has recently been shown to cause inhibition of methanogenic microorganisms in anaerobic sludge when present at low concentrations.

The impact of electrochemical treatment on the susceptibility of PFOS to microbial degradation in anaerobic batch bioassays was investigated. Test solutions containing (partly) electrolyzed PFOS were diluted to minimize microbial inhibition during the biodegradability assays. Monitoring of fluoride release using an ion selective electrode and analysis of fluorinated compounds by high-performance liquid chromatography did not provided evidence that microbial degradation occurred after 9 weeks of incubation. Monitoring will be continued over the coming months. F-NMR measurements will also be performed periodically to determine whether microbial attack leads to a change in the fluorine substitution pattern of the organic molecules in solution.

Results from this study have shown that perfluorobutane sulfonate (PFBS) undergoes electrochemical attack, albeit at considerably lower rates than PFOS. PFBS is a fluorinated derivative proposed as a more environmentally-benign alternative to PFOS. Experiments are being planned to investigate the impact of electrolysis on the susceptibility of PFBS oxidation and reduction products to microbial degradation.

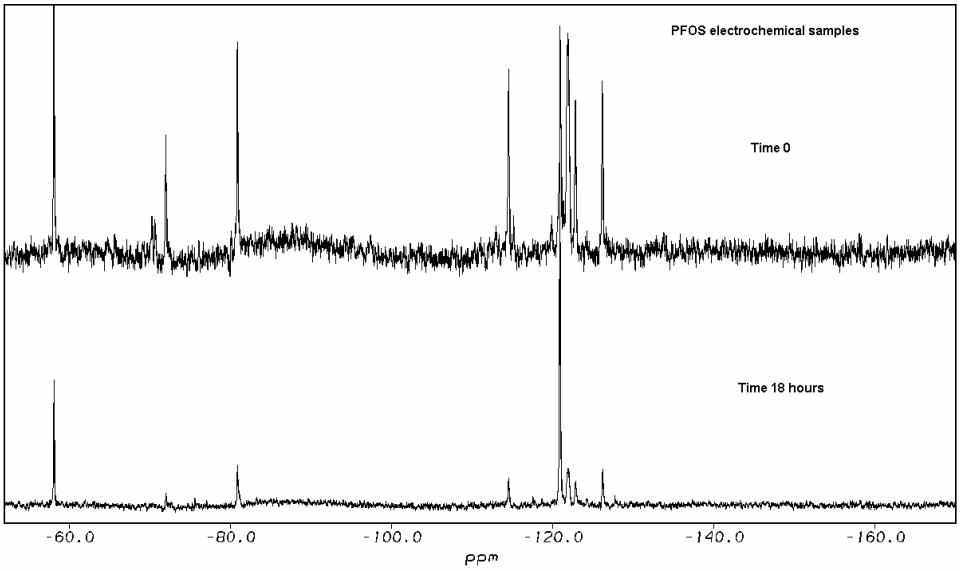

Fig. 2. ^{19}F-NMR of PFOS (lower panel) and PFOS electrolyzed for 18 hours in a BDD batch reactor operated at a current of 10 mA (top panel).

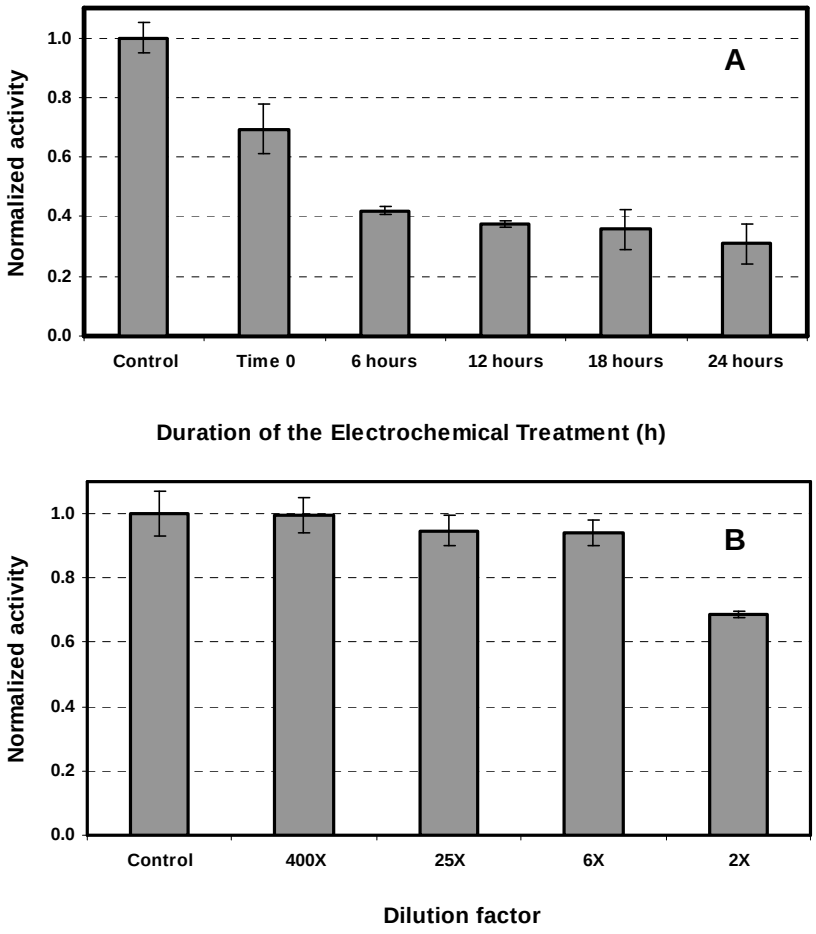

Fig. 3. (**A**) Methanogenic inhibition by PFOS solutions (0.52 mM) subjected to electrochemical treatment for different time periods in a BDD batch reactor. (**B**) Inhibitory effect of PFOS solutions electrolyzed for 24 hours as a function of sample dilution (1x dilution = 0.42 mM).