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.

Background:

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 throughout the globe [1-4]. 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 [5].

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 [6]. Membrane methods [7] and ion exchange [8] are expensive and merely concentrate the aqueous compounds which then require disposal. Additionally, perfluorinated surfactants are not biodegradable in municipal wastewater treatment plants.

Objective and key findings:

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 of PFOS from electrochemical treatment in conventional biological wastewater treatment systems. Perfluorobutane sulfonate (PFBS) is a fluorinated derivative proposed as a more environmentally-benign alternative to PFOS. The impact of electrolysis on the susceptibility of PFBS oxidation and reduction products to microbial toxicity was also investigated in this study.

The results of this study indicate that, regardless of the duration of the electrochemical treatment, the products of the electrolysis of PFOS and PFBS are highly resistant to microbial degradation even after very long periods of incubation, 56 and 34 wks, respectively.

Method of Approach:

Electrochemical treatment: Solutions of PFOS (0.40 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. 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. PFBS electrolysis experiments were performed in a flow-through boron-doped diamond (BDD) electrode reactor at a flow rate of 100 ml/min. PFBS solution (0.4 mM) was electrolyzed at a current density of 2.5 mA/cm^2. Samples (250 ml) of the electrolyzed solution were

collected after 24, 48, 72 and 96 h. An exogenous electrolyte was not added neither to the PFOS nor PFBS solution

Microbial toxicity: The impact of electrochemical treatment on the toxicity of PFAS towards methanogenic microorganisms in anaerobic wastewater treatment sludge was tested in laboratory assays utilizing H_2 as substrate. Control samples were run in parallel during the microbial toxicity assay. The methanogenic activity of the PFAS electrolyzed samples was calculated based on the activity of the control sample.

Anaerobic microbial degradation: Experiments were set up to evaluate the susceptibility to microbial degradation of PFOS and PFBS exposed to electrochemical treatment for different time periods. Bioassays were designed to simulate typical conditions in municipal wastewater treatment plants. Test solutions containing (partly) electrolyzed PFOS or PFBS were diluted by 2-fold to minimize microbial inhibition during the biodegradability assays. Control assays (e.g. abiotic treatments) were run in parallel to account for the loss of the perfluorinated surfactants by mechanisms other than degradation. To promote reductive dehalogenation, hydrogen gas (H_2) was supplied as the electron donor in the full treatment assays. Fluoride concentration using an ion selective electrode and analysis of fluorinated compounds by high-performance liquid chromatography with suppressed conductivity detection and ^{19}F-NMR spectroscopy were performed periodically to determine if the products of PFOS/PFBS electrolysis are susceptible to microbial defluorination.

Technical Results and Data:

Microbial toxicity: The microbial toxicity of PFOS and PFBS was determined in order to ensure that biodegradation assays would be spiked with sub-toxic of these surfactants. Biodegradation assays should be set up under conditions promoting microbial degradation of the target compound.

PFBS (0.4 mM) was not inhibitory to methanogenic microorganisms. Electrochemical treatment of the PFBS solution did only have a minor impact on the specific methanogenic activity. PFBS samples electrolyzed for 72 h or longer did only cause a minor decrease in the methanogenic activity, 24% compared to the uninhibited control. In contrast with PFOS, electrochemical treatment led to an increase in the microbial toxicity of PFOS. The untreated PFOS solution (0.40 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 decreases in the microbial activity ranging from 58 to 70%, depending on the time of electrolysis. The observed microbial inhibition should be attributed to products from the electrolysis of PFOS, including fluoride. Fluoride has recently been shown to cause inhibition of methanogenic microorganisms in anaerobic sludge when present at low concentrations.

Based on these results, test solutions containing (partly) electrolyzed PFOS or PFBS were diluted by 2-fold to minimize microbial inhibition during the biodegradability assays.

Microbial degradation of electrolysis products:
The impact of electrochemical treatment on the susceptibility of PFOS and PFBS to microbial degradation was investigated in anaerobic batch bioassays. Electrolyzed PFOS and PFBS samples collected at regular intervals for up to 24 and 100 h, respectively, were tested for biodegradation potential.

For PFOS, the concentration of total organic carbon (TOC) detected in solution at the different times of electrolysis exceeded the residual surfactant concentration, suggesting some accumulation of electrolysis products in solution. The TOC and PFOS in the solution electrolyzed for 24 h were 0.10 and 0.25 mM. Nonetheless, fluorinated compounds other than PFOS were not detected by F-NMR, mass spectroscopy, or ion

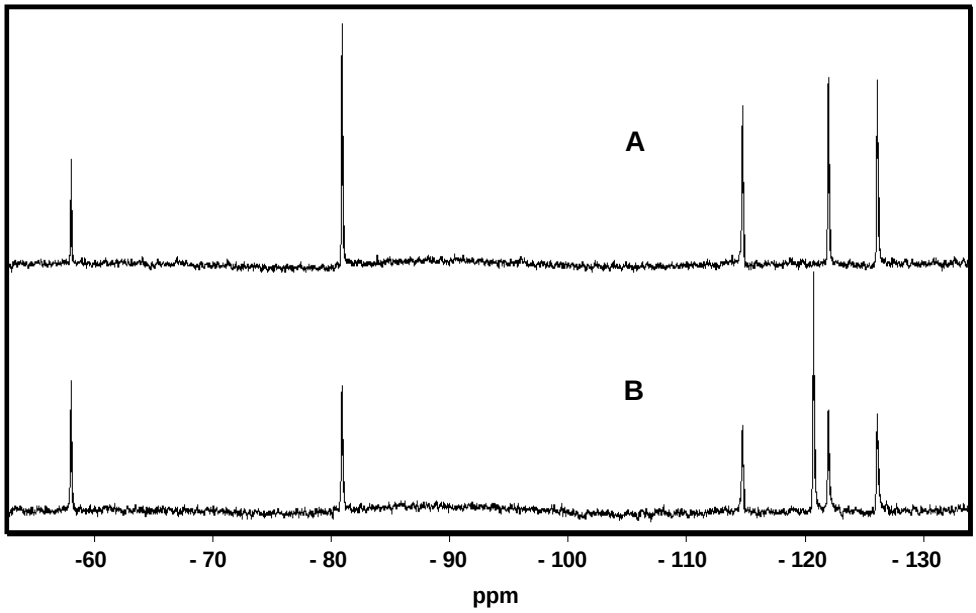

Figure 2. *^{19}F-NMR of (A) PFBS and (B) PFBS subjected to electrochemical attack for 24 h in a BDD flow-through reactor operated with a current density of 2.5 mA/cm^2. All chemical shifts were reference to the internal standard 4'-(trifluoromethoxy)-acetanilide 4-TFMeAc (-58.08 ppm) [9].*

chromatography measurements in the sample electrolyzed for 18 h (Fig. 1). The F-NMR spectrum of treated PFOS only shows a new peak with a shift of approximately -120.5 ppm with respect to that of untreated PFOS which corresponds to the fluoride ion.

In the case of PFBS, the residual concentration of surfactant and TOC in solution was nearly the same independently of the electrolysis time, indicating complete mineralization of the compound by electrolysis. After 72 h of electrolysis, only traces of both TOC and surfactant were detected. These results are in agreement with ^{19}F-NMR measurements which showed that PFBS was the only fluorinated compound detected in all the electrolyzed solutions. The only new peak detected in the F-NMR spectrum of electrolyzed samples corresponded to the fluoride ion (Fig. 2).

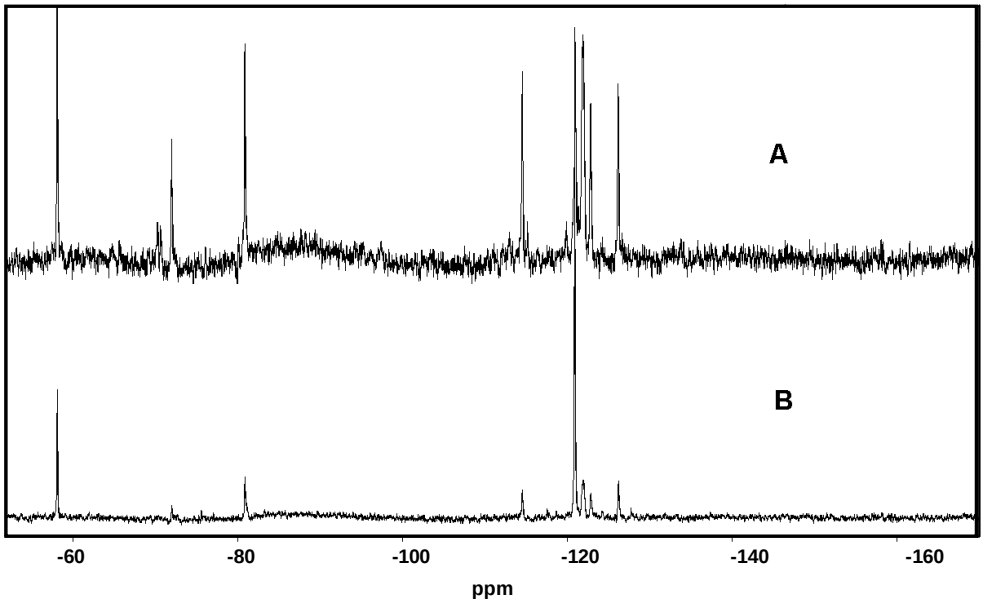

Figure 1. *^{19}F-NMR of (A) PFOS and (B) PFOS subjected to electrochemical attack for 18 h in a BDD batch reactor operated at a current of 10 mA.*

Regardless of the duration of the electrochemical treatment, the products of the electrolysis of PFOS and PFBS were found to be highly resistant to microbial degradation after very long periods of incubation, 56 and 34 wks, respectively. Fluoride release, mass spectroscopy, ion chromatography and ^{19}F-NMR measurements in the samples did no provide any evidence that microbial attack led compound mineralization, or to changes in the fluorine substitution pattern of the organic molecules. A small decrease in the concentration of PFOS and PFBS was observed during the first weeks of the experiment in assays inoculated with either killed- or live sludge can be attributed to the partial sorption of the surfactants to the biomass.

References

1. **Kannan, K., et al**. 2004. Perfluorooctanesulfonate and related fluorochemicals in humand blood from several countries. *Environ. Sci. Technol*. 38(17):4489 - 4495.

2. **Giesy, J.P. and K. Kannan.** 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol*. 35(7):1339 - 1342.

3. **Martin, J.W., et al.,** 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Artic. *Environ. Sci. Technol*. 38(2): p. 373 - 380.

4. **Houde, M., et al.**, 2006. Biological monitoring of polyfluoroalkyl substances: a review. *Environ. Sci. Technol*. 40(11): p. 3463 - 3473.

5. **Martin, J.W., et al.,** 2004. Analytical challenges hamper perfluoroalkyl research. *Environ. Sci. Technol*. 38(13): p. 248A - 255A.

6. **Kissa, E.,** Fluorinated Surfactants and Repellants. 2001, New York: Marcel Dekker, Inc.

7. **Tang, C.Y., et al.,** 2006. Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater. *Environ. Sci. Technol*. 40(23): p. 7342 - 7349.

8. **Lampert, D.J., et al.,** 2007. Removal of perfluorooctanoic acid and perfluorooctane sulfonate from wastewater by ion exchange. practice period. Hazard., Toxic, Radioact. Waste Manag. 11:60 - 68.

9. **Tugnait, M., et al.** 2002. The metabolism of 4-trifluoromethoxyaniline and [^{13}C]-4-trifluoromethoxyacetanilide in the rat: detection and indentification of metabolites excreted in the urine by NMR and HPLC-NMR. *J. Pharmac. Biomed. Anal.* 28:875 - 885.