Task ID: 425.018
Task Title: Destruction of Perfluoroalkyl Surfactants in Semiconductor Process Waters Using Boron Doped Diamond Film Electrodes
Deliverable Title: Report on the susceptibility of a variety of PFAS compounds to electrolysis at BDD anodes and cathodes

Summary Abstract:
Perfluoroalkyl surfactants (PFAS) are non-biodegradable compounds that have been found in the blood of humans and animals around the world. The presence of these compounds in the environment is reason for concern. As a result of this the EPA has restricted the use of PFAS to the semiconductor industry.

The semiconductor industry uses PFAS for electroplating and electronic etching baths, as well as a photographic emulsifier. Expensive membrane and ion exchange methods can be used to remove the PFAS from waste streams. This concentrated PFAS can be dissolved in certain solvents and disposed of by incineration. Currently there is no efficient method for destructive removal of PFAS from wastewater streams.

Advanced Oxidation Processes (AOPs) are typically used to degrade non-fluorinated organic compounds. However, the stable carbon-fluoride bonds in PFAS react slowly in conventional AOP methods. Therefore, AOPs using UV light with TiO_2 photocatalysts or peroxide, or ozone/peroxide systems, are inefficient methods of PFAS destruction.

The objective of this investigation is to determine if Boron Doped Diamond (BDD) Film Electrodes may be used to efficiently degrade PFAS in water. BDD electrodes offer many advantages over other materials including: high resistance to fouling by chemisorbed metals or other impurities, very low catalytic activity for oxygen and hydrogen evolution and resistance to chemical attack.

The optimal conditions for oxidation and reduction of Perfluorooctane Sulfonate (PFOS) and Perfluorobutane Sulfonate (PFBS), using BDD electrodes will be determined. This will involve determining the effect of electrode potential, solution pH, reactant concentration, temperature, and electrolysis time. Oxidation and reduction products for the target compounds at BDD anodes and cathodes will be determined. These studies will be performed in both flow-through reactors with parallel plate electrodes and batch reactors using a rotating disk electrode (RDE) and results will be compared to determine mass transfer effects.

Technical Results and Data:
Electrolysis experiments were conducted in flow-through and batch reactors. The flow-through reactor has an anode surface area of 25 cm^2 and a bed volume of 20 mL, yielding a surface area to solution volume ratio of 1.25 cm^2/mL. The batch reactor has 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. Reaction rates in the flow-through reactor are representative of those attainable in a real water treatment unit operation.

Current densities ranging from 2.5 to 20 mA/cm^2 were applied to a BDD electrode immersed in 0.4 mM solutions of PFOS or PFBS. Samples were taken at different times while holding the current density constant. PFOS or PFBS concentrations in the solutions were determined using a High Performance Liquid Chromatography

(HPLC) equipped with a conductivity detector. Total Organic Carbon (TOC) was determined for each set of samples to compare the carbon and PFAS removal. An ion chromatograph was used to determine the amount of sulfate and fluoride being released into the solution during the oxidation process.

Electrolysis experiments using the flow through BDD reactor indicate that PFOS can be rapidly removed from water. Figure 1 shows the PFOS and total organic carbon (TOC) concentrations as a function of treatment time. Reaction rates for PFOS and TOC were first order with respect to concentration, with a treatment half-life of less than 10 minutes.

Figure 1. PFOS and TOC concentrations as a function of treatment time in the flow through reactor operated at a current density of 15 mA/cm^2.
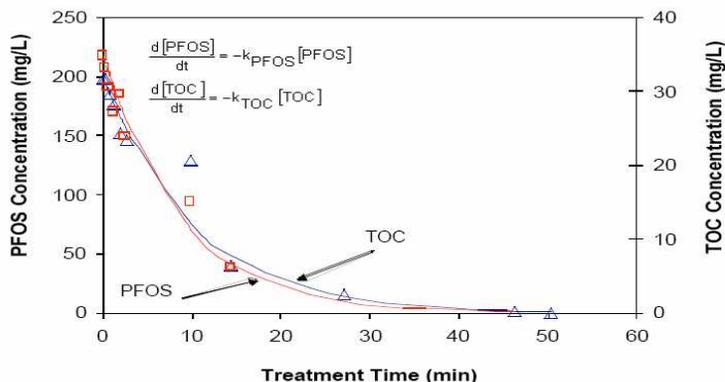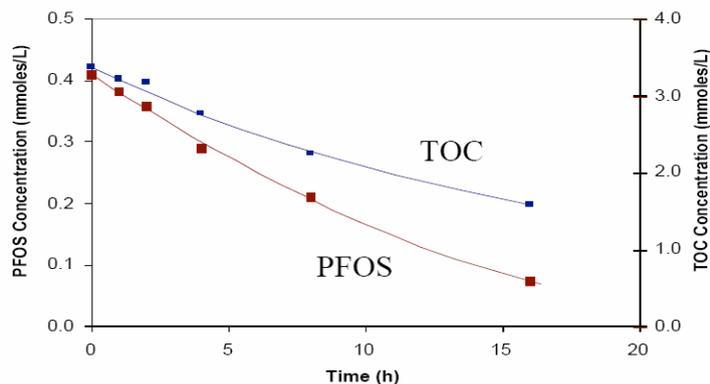
$$\frac{d[PFOS]}{dt} = -k_{PFOS}[PFOS]$$

$$\frac{d[TOC]}{dt} = -k_{TOC}[TOC]$$

Figure 2. PFOS and TOC concentrations in the batch reactor operated at a current density of 10 mA/cm^2.

The near identical declines in PFOS and TOC concentrations in Figure 1 indicates that PFOS oxidation at a current density of 15 mA/cm^2 does not produce reaction products that build-up in the solution. However, at lower current densities, TOC removal rates were slower than those for PFOS. Figure 2 compares PFOS and TOC removal in a batch reactor and shows that the removal half-life for TOC removal of 16 hours is approximately twice the 8 hour removal half-life for PFOS.

Sulfate analyses showed that one sulfate evolved in the solution for every PFOS molecule degraded. Fluoride analyses indicated that an average of 4.5 fluoride ions were released per PFOS molecule degraded. This indicates that TOC in the form of PFOA, PFHtA and PFHxA was removed from the solution via volatilization. The fluoride mass balance indicates that volatilization of PFHxA was the primary factor removing TOC from the solution.

PFOS removal rates were independent of the applied potential for current densities of 5 mA/cm^2 or greater. Figure 3 shows that PFOS removal at 2.5 mA/cm^2 was slightly slower than removal rates at 5 & 15 mA/cm^2, which were identical. This suggests that the reaction mechanism involves indirect PFOS oxidation by hydroxyl radicals produced from water oxidation, rather that direct oxidation of PFOS at the electrode surface. This conclusion is consistent with other investigations of organic compound oxidation at BDD electrodes.

Figure 3. PFOS concentration versus time in the batch reactor for current densities of 2.5, 5 and 15 mA/cm^2. Lines are fits of the kinetic model.
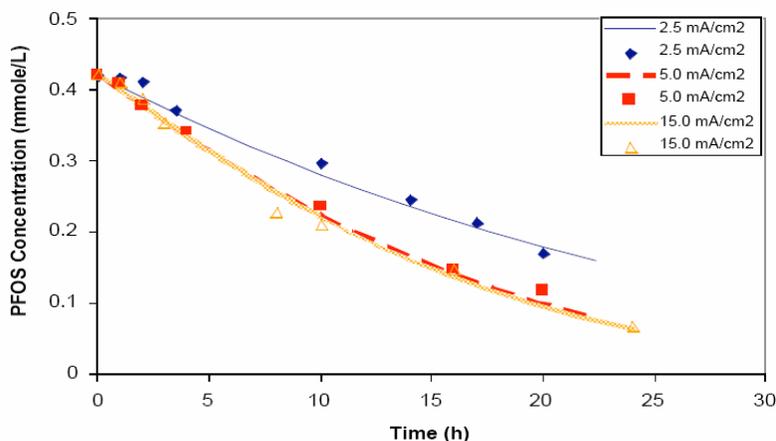
TOC removal rates were dependent on the electrode potential and increased with increasing current density, as shown in Figure 4. In contrast to the identical PFOS removal rates at 5 & 15 mA/cm^2, Figure 4 shows that the TOC removal half-life at 15 mA/cm^2 was ~25% greater than that at 5 mA/cm^2.

Figure 4. TOC concentration versus time in the batch reactor for current densities of 2.5, 5 and 15 mA/cm^2. Lines are fits of the kinetic model.
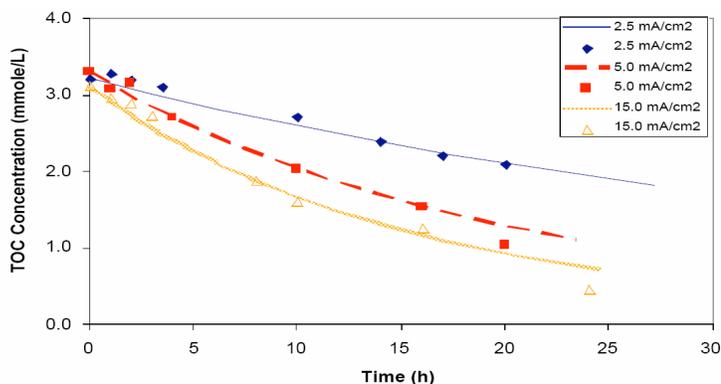
Electrolysis experiments were performed in a batch reactor for PFBS. Figure 5 shows the decline of PFBS versus time for different current densities and demonstrates that PFBS can be removed from water by electrochemical oxidation process. The PFBS concentration follows a linear trend as time elapses, indicating a zero order reaction with respect to PFBS concentration in the solution. Figure 5 also shows that the PFBS degradation rate increases with increasing current density. After 100 hours the PFBS removal is 29% for a current density of 5 mA/cm^2 while the removal is 91% for 20

mA/cm^2. These results suggest that the PFBS reaction is dependent on the electron transfer process at the electrode surface.

Figure 5: PFBS concentration versus the time in the batch reactor for current densities of 5, 10, 15, and 20 mA/cm^2. Lines are linear fits of the data.
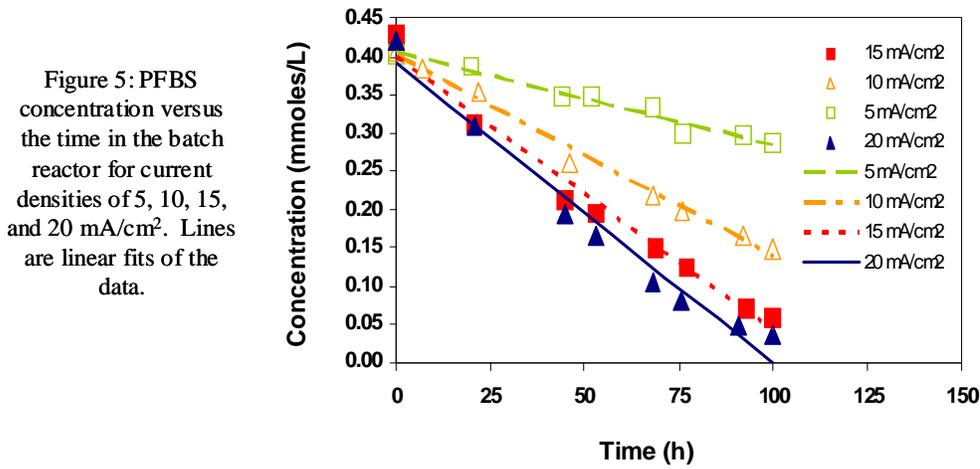

Figure 6 shows the fluoride concentration evolved versus time for different current densities, and figure 7 shows the sulfate concentration as a function of time for different current densities. Both fluoride and sulfate concentration produced follows zero order as indicated by the linear increase as a function of time. The formation rates for both fluoride and sulfate increase with current density, which is consistent with those observed for PFBS degradation.
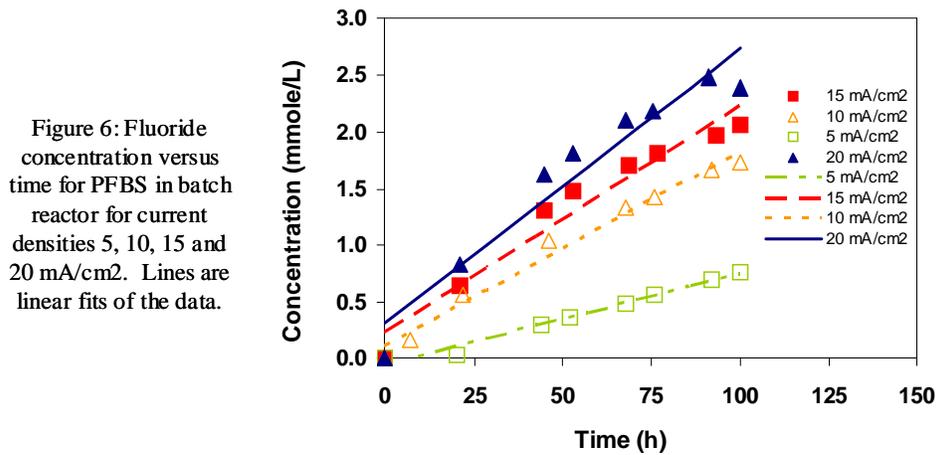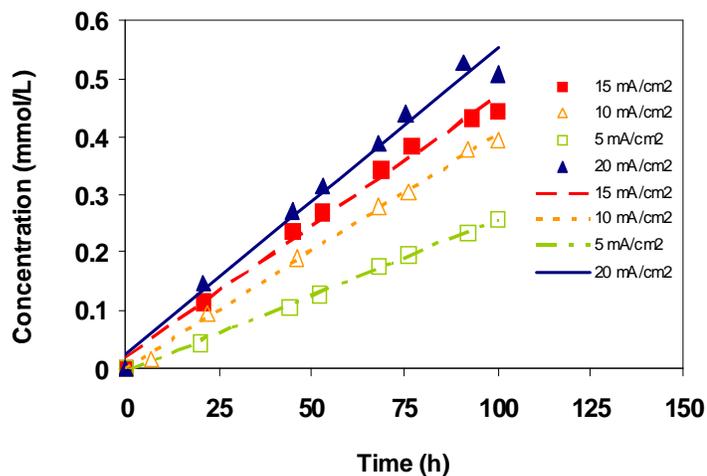
Figure 6: Fluoride concentration versus time for PFBS in batch reactor for current densities 5, 10, 15 and 20 mA/cm2. Lines are linear fits of the data.

Figure 7: Sulfate concentration versus time for PFBS in batch reactor at current densities of 5, 10, 15, and 20 mA/cm2. Lines are linear fits of the data.

Future Work:

Electrolysis experiments will be performed on PFBS using the flow through reactor to determine the mass transfer effects. The effects of temperature and pH will be investigated for both PFBS and PFOS. Degradation products generated under different treatment conditions (*e.g.* current density, electrolysis time, pH) will be determined. Current efficiency and cost effectiveness will be analyzed for both PFOS and PFBS.