Task ID: 425.018

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

Deliverable: Report on a prototype PFAS concentrator and electrochemical reactor for pilot testing on real semiconductor wastewaters containing both high and low concentrations of PFAS compounds

Summary Abstract:

Perfluoroalkyl surfactants or PFAS are used in a wide variety of processes in the semiconductor industry. These surfactants have been discovered in the blood of human beings and wildlife in different parts of the world making them a major concern. PFAS compounds tend to be very stable and do not degrade using Advanced Oxidation Processes (AOP). Electrochemical oxidation of PFAS has been shown to be an effective method for destroying these compounds in aqueous streams. However, most industrial waste streams contain dilute amounts of PFAS compounds, as well as large amounts of water. Concentrating the PFAS compounds and decreasing the amount of water that would need to be treated is a more practical technique.

The objectives of this task include: 1) to determine the most effective method for concentrating the target compounds from dilute aqueous solutions; 2) to determine the adsorption isotherms for target compounds as a function of solution pH and ionic strength using different types of adsorbents; 3) to determine mass transfer characteristics using column breakthrough experiments; and 4) to design and test a prototype PFAS concentrator and electrochemical reactor on semiconductor wastewaters. Thus far adsorbents have been tested for the concentration of PFAS compounds which will be discussed in the Technical Results and Data.

Technical Results and Data:

An anion exchange resin, NaY80, and a zeolyte, CBV28014, were tested to determine if PFOS would adsorb to the available sites on the resin. 1.0 to 4.9 g/L of NaY80 or CBV28014 were added to PFOS solutions with concentrations of 7 to 250 mg/L of PFOS. Solutions were placed in a Koolatron PC3 at 22^oC for 24 hours. Samples were taken and analyzed for Total Organic Carbon (TOC). The TOC concentration was used to determine the amount of PFOS adsorbed to each type of adsorbent. No PFOS was adsorbed to the CBV28014. There was over 100 mg of PFOS adsorbed to 1 g of NaY80. Figure 1 shows the isotherm for the NaY80 anion exchange resin.



Figure 1: PFOS isotherm for anion exchange resin NaY80.

Figure 2 shows the isotherm for granular activated carbon (GAC) F400. The GAC has a better loading capacity than the NaY80 zeolite.



Figure 2: PFOS isotherm for granular activated carbon F-400.

Another anion exchange resin IRA 458 was also tested to determine if a better loading of PFOS could be achieved. 6L of 10 mM NaClO4 solution was added to a 6 L flask. 10 g of IRA 458 were added to the solution and allowed to stir overnight to equilibrate the resin with the solution. 200 mg of PFOS were added to the solution and the solution was stirred overnight. A sample of PFOS was then taken, and 200 mg of PFOS was added to the solution. This procedure was repeated until 12 g of PFOS were added to the solution. The same experiment was also performed for PFBS. Samples were tested for aqueous concentration and a mass balance was performed to determine the concentration on the ion exchange resin. Figure 3 shows the isotherms for the PFOS and PFBS that was obtained using the IRA 458 ion exchange resin.



Figure 3: PFOS and PFBS isotherms using ion exchange resin IRA 458.

Comparing the three different isotherms we find that the IRA 458 has a better loading capacity for the PFOS. The IRA 458 takes up 4 times more PFOS than PFBS.

Studies were performed at different temperatures for both the GAC and the IRA 458. Figure 4a and b show that PFOS more readily adsorbs to both the GAC and the IRA 458 as the temperature of the solution increases. This was also the case for the PFBS isotherms at different temperatures.



Figure 4a: PFOS isotherms for different temperatures using ion exchange resin, IRA



Figure 4b: PFOS isotherms for different temperatures using granular activated carbon, F400.

Kinetic studies were performed to determine the mass transfer rate of PFOS onto an ion exchange resin and GAC. Two 6 L solutions containing 200 mg/L PFOS and 10 mM NaClO4 electrolyte solution were made up and 10 g of either the GAC or IRA 458 were added to the solutions. Samples were taken over a time. These studies were used to help determine which adsorbent would be beneficial in concentrating PFOS. Figure 5 shows the concentration of PFOS as a function of time after the addition of 10.0 grams of GAC or ion exchange resin. This study shows that PFOS is more readily adsorbed on to the ion exchange resin than the GAC. The study also shows that almost all of the PFOS is removed after 5 hours using the ion exchange resin. A similar experiment was performed for the PFBS. Figure 6 shows that the GAC is better suited for removing PFBS from solution. Half of the PFBS was removed from the solution after 2 days while only 25 percent of the PFBS was removed using the IRA 458.



Figure 5: Concentrations of PFOS left in the solution as a function of time for ion exchange resin and granular activated carbon.



Figure 6: Concentrations of PFBS left in the solution as a function of time for ion exchange resin and granular activated carbon.

Future Work:

Column breakthrough experiments will also be performed to determine the mass transfer characteristics for the best performing adsorbents or ion exchange resins. Regeneration of the adsorbent will be performed using solutions at different pH and temperatures to determine the best way to desorb the PFOS from the GAC or IRA 458. Design and implementation of a prototype PFAS concentrator and electrochemical reactor on semiconductor wastewaters will be undertaken.