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 effectiveness of different adsorbents and ion exchange resins for concentrating PFAS compounds from dilute wastewater streams

Summary Abstract:

Perfluorooctyl sulfonate (PFOS) and other perfluoroalkyl sulfonate (PFAS) compounds are widely used in semiconductor manufacturing. Presently, there are no effective treatment methods for the removal of PFAS compounds from wastewater streams.

The objective of this task is to determine the most effective method for concentrating PFAS compounds from dilute aqueous solutions. To accomplish this, adsorption isotherms for PFAS compounds will be determined on several activated carbons, hydrophobic zeolites and ion exchange resins over a range of solution pH values and ionic strength. The mass transfer characteristics of the most effective adsorbents will be determined using column breakthrough experiments.

Technical Results and Data:

Adsorption isotherms for PFOS have been determined on an MFI zeolite and a FAU zeolite. The MFI zeolite had a silica to alumina (Si/Al) ratio of 500 and the FAU zeolite had a Si/Al ratio of 80. The isotherms were measured at 22 °C in deionized water at neutral pH. The samples were equilibrated for 24 hours and solution concentrations of PFOS were determined via Total Organic Carbon (TOC) analysis. The Freundlich isotherm model was used to fit the experimental data. The Freundlich model describes the adsorbed concentration (C_s) as a function of the aqueous concentration (C_{aq}), the Freundlich capacity coefficient (K_F), and the Freundlich exponent (n), is given by:

$$C_{\rm s} = K_{\rm F} C_{\rm aq}^{1/n}$$

Figure 1 compares adsorption of PFOS on the two zeolites with a PFOS isotherm measured for Calgon F-400 granular activated carbon. There was no measurable PFOS adsorption on the MFI zeolite. This can be attributed to size exclusion of the PFOS molecule by the ~5.5 Å pore opening in the MFI. The FAU zeolite with a 7.8 Å diameter pore opening adsorbed PFOS, but not as much as the F-400 activated carbon.

The most important difference between the FAU and F-400 isotherms was the uptake at low PFOS concentrations. Table 1 compares the isotherm parameters for the FAU and F-400 adsorbents. The smaller isotherm exponent for the F-400 suggests that it will be a much better adsorbent than the FAU for aqueous concentrations below those shown in Figure 1. Removal of PFAS compounds at low aqueous concentrations is especially important in the semiconductor industry.

Parameter	FAU	F-400
n	0.7627	0.289
K _F	2.77	60.9

Table 1. Freundlich isotherm parameters for FAU and Calgon F-400 adsorbents at 22 °C in neutral pH deionized water.



Figure 1. Comparison of PFOS adsorption on MFI and FAU zeolites and activated carbon at 22 °C in neutral pH deionized water.

Future Work:

Adsorption isotherms for PFOS will be measured on several anion exchange resins at neutral pH in deionized water. These isotherms will be compared to those for the FAU and F-400 adsorbents. Adsorption isotherms for other PFAS compounds will then be measured over a range of temperatures, pH and ionic strength for the two most promising adsorbents. Subsequently, the mass transfer characteristics for the two most promising adsorbents will be compared using column breakthrough experiments.