Chemical Engineering Thesis Defense

Catalytic Treatment of Per- and Polyfluoroalkyl Substances (PFAS) in Semiconductor Wastewaters

School for Engineering of Matter, Transport and Energy

Alec B. Nienhauser

Advisor: Paul Westerhoff

Abstract

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic chemicals used for a wide variety of products and industrial processes, including being an essential class of chemicals in the fabrication of semiconductors. Proven concerns related to bioaccumulation and toxicity across multiple species has resulted in health advisory and regulatory processes initiated for PFAS in drinking and wastewaters. Among impacted users of PFAS, the semiconductor industry is in urgent need of technologies to remove PFAS from water. Specifically, they prefer technologies capable of mineralizing PFAS into inorganic fluoride (F-). The goal of this thesis is to compare the effectiveness of photo- versus electro-catalytic treatment in benchtop reactor systems on long- and short-chain PFAS in industrial wastewater before selecting one technology to investigate comprehensively. First, a model wastewater was developed based upon semiconductor samples to represent water matrices near the tool where PFAS are used and the aggregate Fab (Fabrication facility) wastewater effluent, which were then used in batch catalytic experiments. Second, batch experiments with homogenous photocatalysis (UV/SO32-) were found to be more energy intensive than heterogeneous catalysis using boron doped diamond (BDD) electrodes, and the latter approach was then studied in-depth. During electrocatalysis, longer chain PFAS (C8; PFOA & PFOS) were observed to degrade faster than C6 and C4 PFAS. This study is the first to report near complete defluorination of not only C8and C6- PFAS, but also C4-PFAS, in model wastewaters using BDD electrocatalysis, and the first to report such degradation in real Fab wastewater effluents. Based upon differences in PFAS degradation rates observed in single-solute systems containing only C4 PFAS versus multi-solute systems including C4, C6 and C8 PFAS, it was concluded that the surfactant properties of the longer-chain PFAS created surface films on the BDD electrode surface which synergistically enhanced removal of shorter-chain PFAS. The results from batch experiments that serve as the basis of this thesis will be used to i) assess the chemical byproducts and their associated bioaccumulation and toxicity. This thesis was aimed at developing an efficient method for the degradation of perfluoroalkyl substances from industrial process waters at realistic concentrations. After investigating both photo- and electrocatalytic systems, electrochemical degradation was studied in extensively in order to explore the future of electrocatalytic systems for PFAS degradation. A pilot scale study using two BDD electrodes was used to conduct three-to-five-hour experiments on model and real industrial wastewater (IWW) solutions. BDD electrodes were capable of degrading both longand short-chain PFAS at 100 mA/cm2 and 3 cm2 of electrode area. The kinetics was faster for long-chain PFAS over medium-chain PFAS, which were faster than short-chain PFAS. Overall, BDD electrodes were able to reach 90% defluorination of PFAS in five hours and displayed potential for future scale-up reactor systems.