Adsorption of Perfluoroalkyl Substances with Activated Carbon:

Characterizing Non-hazardous Simulants

AFIT POCs: Jennifer Hensley*, Kyle Eckhoff, and Dr. Willie F. Harper, Jr.   EPA/ORD POC: Matthew Magnuson

*AFIT Research Assistant and MS Student at Wright State University, Fairborn, OH

United States Environmental Protection Agency

Air Force Institute of Technology

Introduction

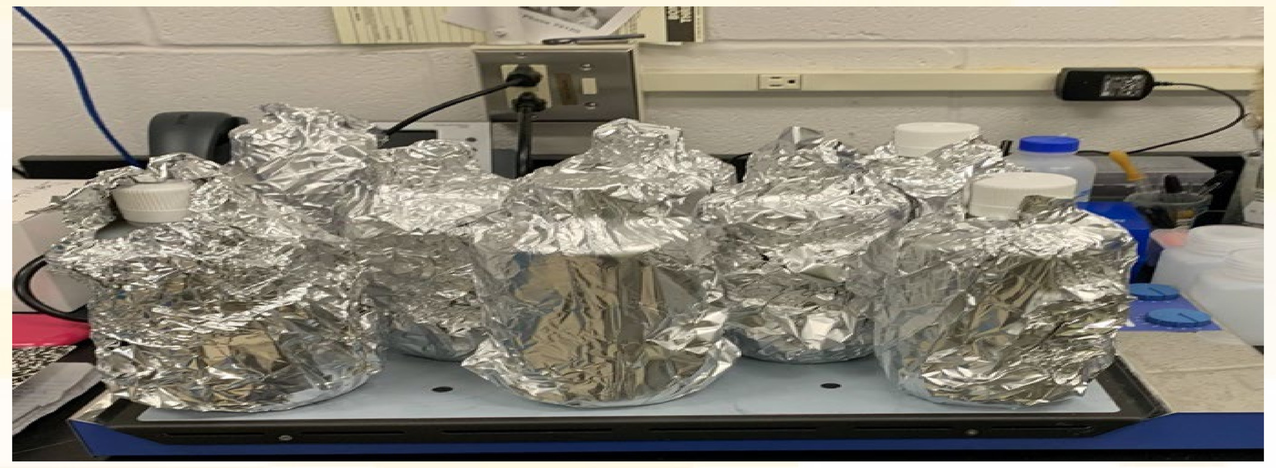
PFAS are a category of manufactured chemicals that have been used in industry and consumer products since the 1940s. There are thousands of PFAS chemicals, and they are found in many different consumer, commercial, and industrial products. PFAS have characteristics that make them useful in a variety of products, including nonstick cookware, waterproof clothing, and firefighting foam, as well as in certain manufacturing processes. PFAS tend to break down extremely slowly in the environment and can build up in people, animals, and the environment over time. Even though some specific PFAS have been largely phased out due to health and environmental concerns, they may still be found in the environment and in drinking water (https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas). EPA's proposed drinking water regulation include 6 PFAS: PFOA, PFOS, PFHxS, PFNA, PFBS, HFPO-DA.

Motivation

Simulants could facilitate treatment studies of PFAS, reducing cost, timeline, and safety concerns. This study used powdered activated carbon batch experiments and artificial neural networks (ANN) to access allura red, tartrazine, and indigo carmine as simulants for PFOA, PFOS, and other PFAS species. These 3 non-hazardous food dyes have similar functional groups and anionic charges, to that of PFOA and PFOS, two of the most well-known toxic PFAS chemicals. Powdered Activated Carbon (PAC) is among the most cost effective and time efficient treatment processes available for PFAS remediation. Artificial neural networks are a tool that can be utilized to help predict which chemicals can serve as simulants for PFAS species.

Methods

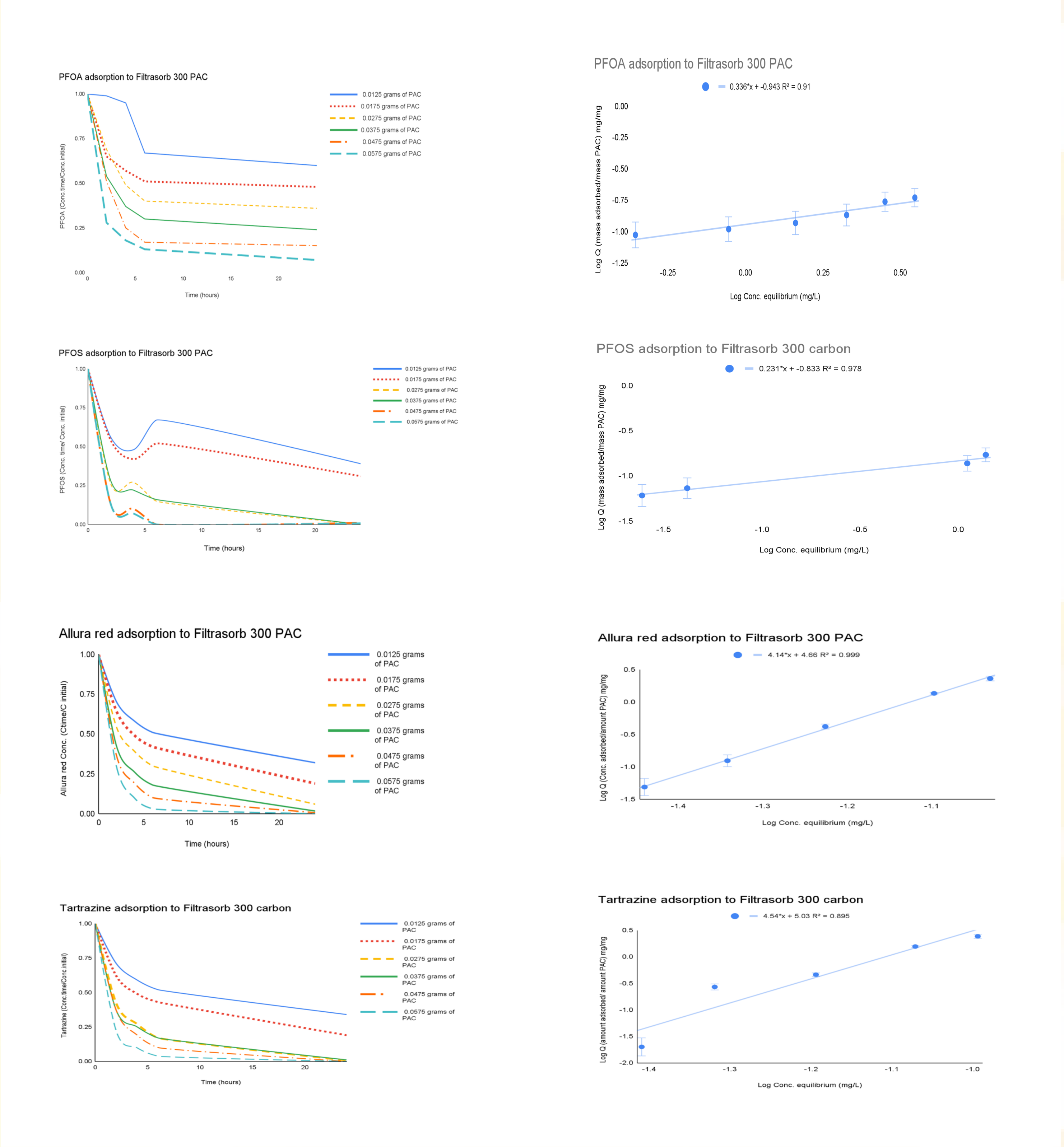
A 0.014 mM solution of tartrazine, indigo carmine, allura red, PFOA, PFOS, or PFAS rinse water from a firefighter hanger that had been decontaminated was treated with 6 different PAC amounts, ranging from 0.0125 – 0.0575 grams over 24 hours. UV- Vis spectrometer was used to detect the food dyes, while liquid chromatograph/solid-phase extraction was used for PFAS detection in water. SEM and EDS were used to analyze PAC surfaces before and after treatment. Artificial neural networks were used to correlate 16 pubically available molecular descriptors with K_d values. The simulants were classified as poor (K_d < PFAS K_d), suitable (K_d = PFAS K_d), or conservative (K_d > PFAS K_d).



Key results

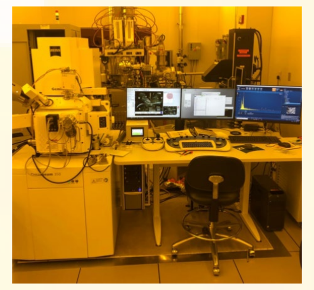
1. Indigo carmine was a suitable simulant for PFOS and conservative simulant for PFOA. Tartrazine and allura red were both conservative simulants for PFOA and PFOS.
2. The SEM and EDS revealed fluorine and sulfur functional groups attached to PFAS treated carbon. Food dyes showed active sodium groups attached to the carbon surface.
3. The ANN predicted all food dyes would be conservative simulants for PFBA, PFBS, and PFHpA.

Powdered activated Carbon adsorption of PFAS and dyes

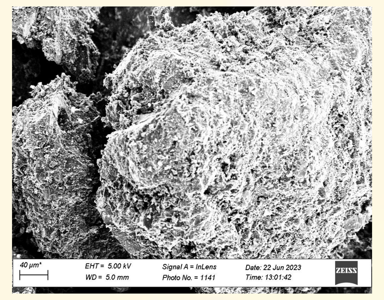


Carbon surface analysis

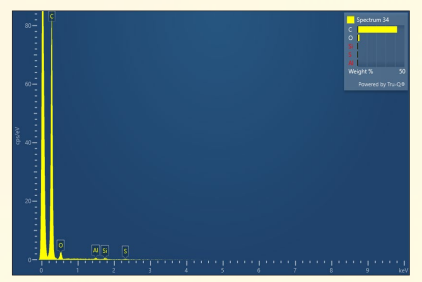
Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) of before and after treatment of PFAS rinse water with powdered activated carbon



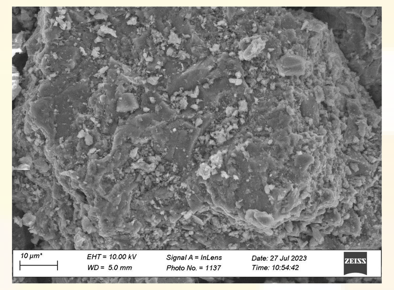
SEM/EDS



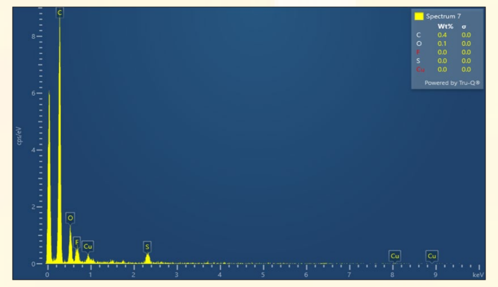
SEM image before treatment



EDS spectrum before treatment



SEM image after treatment

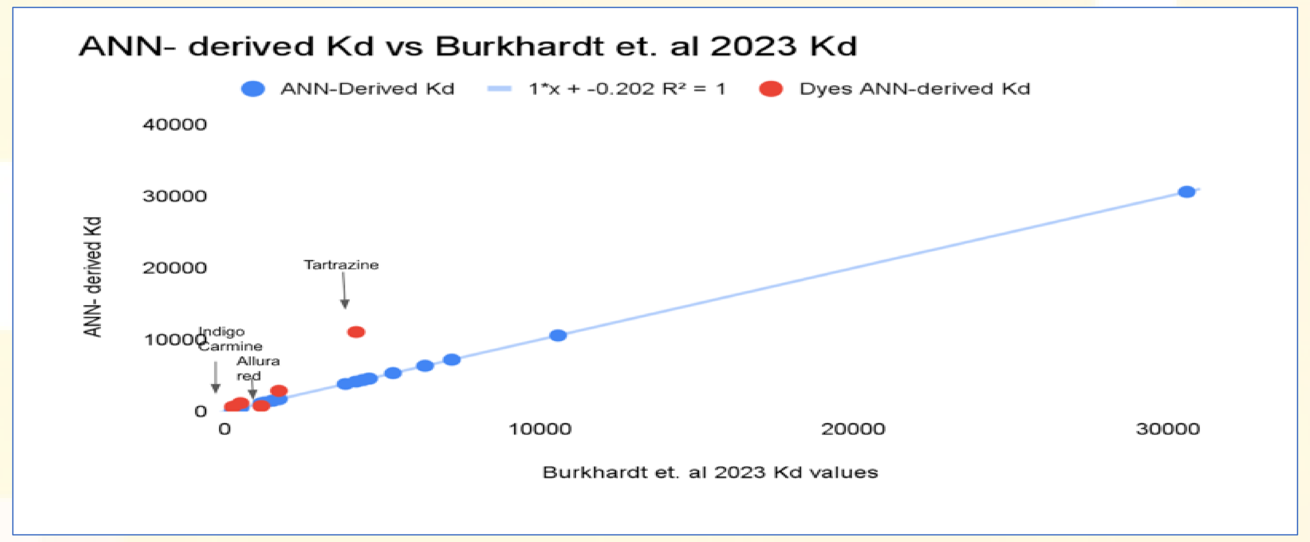


EDS spectrum after treatment

Artificial neural networks (ANN)

Inputs → Hidden layers → K_d predictions

Molecular descriptors are inputs put into the network that assigns various weights through multiple layers that contain various functions. Credible publicly available K_d values are used to train the network to predict non-hazardous food dyes as simulants for multiple PFAS species. With 5 hidden layers used in the ANN, it can show direct strong linear correlation of what the ANN is able to predict compared to the literature K_d values measured.



Dye being tested	ANN-derived Kd	Experimental Kd	ANN classification of PFAS species
Allura red	1174	45708	Conservative: PFBA, PFBS, PFHpA & PFPeA Poor: PFHxA, PFTA, PFOA, PFPeS, PFHpS, PFOS, PFNA, PFDA 4:2 FTS, 6:2 FTS, 8:2 FTS
Indigo carmine	655	0.133	Conservative: PFBA, PFBS, and PFHpA Poor: PFPeA, PFHxA, PFTA, PFOA, PFPeS, PFHpS, PFOS, PFNA, PFDA 4:2 FTS, 6:2 FTS, 8:2 FTS
Tartrazine	11079	107151	Conservative: PFBA, PFBS, PFPeA, PFHxA, PFHpA, PFOA, PFPeS, PFHpS, PFOS, PFNA, PFDA 4:2 FTS, 6:2 FTS, 8:2 FTS Poor: PFTA

Takeaways

- Indigo carmine could be used as a simulant for PFOA and PFOS during wastewater treatment testing.
- In wastewater that contains multiple PFAS species, competitive adsorption can affect how well different PFAS species adsorb to carbon making adsorption capacities and rates of remediation uncertain.
- Artificial neural networks can be used as a tool in water quality to help predict contaminants abilities to be removed but must have reliable data for training.