Evaluation of Anionic Dyes as Proxies for Sorption of PFAS onto Strong Base Anion Exchange Resins

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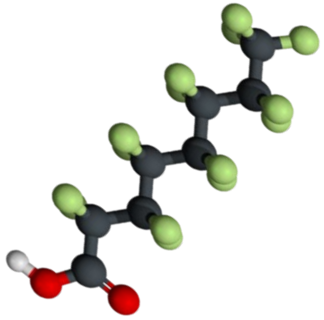
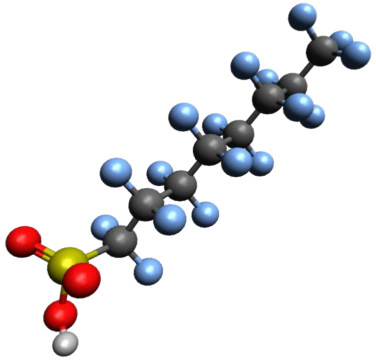
Anion Exchange Resin (AER)



Perfluorooctanoic acid (PFOA)



Perfluorooctanesulfonic acid (PFOS)

Team Members

- Experimental Team
  - Lee Heckman
  - Donald Schupp
  - Nicole Sojda
- Resin Conditioning
  - Cameron Gastaldo
  - Brooke Gray
  - Esther Hughes
  - Sophia Pedigo
  - Samantha Smith
  - Eva Stebel
- Modeling and Design
  - Boris Datsov
  - Levi Haupert
  - Matthew Magnuson

Why Dyes?

- PFAS analysis is expensive and can take months to get results!
- Spectrophotometer measurements are inexpensive and convenient.
- Dyes that behave similarly to PFAS could be used for:
  - Screening experimental designs
    - Batch tests
    - Rapid small-scale column tests
  - Estimating treatability of waters
  - Investigating fundamentals of adsorption on ion exchange resins

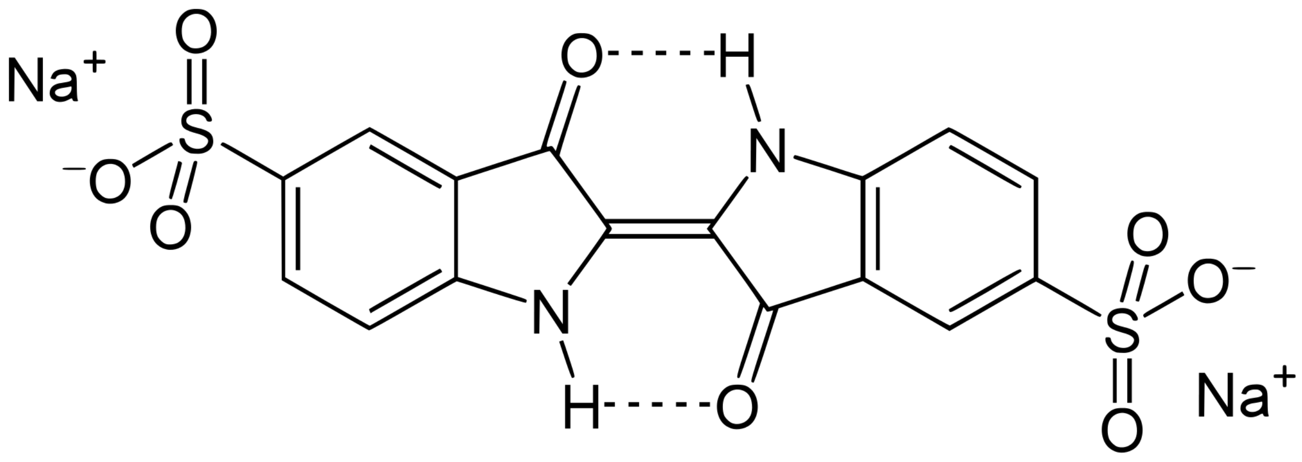
Background

- Sörengård, et al. correlated dyes and PFAS on several sorbents.
- Ion exchange resins not included.
- Three of four dyes studied by Sörengård will not work for ion exchange resins.
  - Cationic
  - Vulnerable to pH changes or aggregation
- Remaining dye, indigo carmine, is divalent, while most PFAS of interest are monovalent.
- Makes modeling more complicated, but not a deal- breaker.
- Finding a monovalent, anionic dye to the study would be ideal.

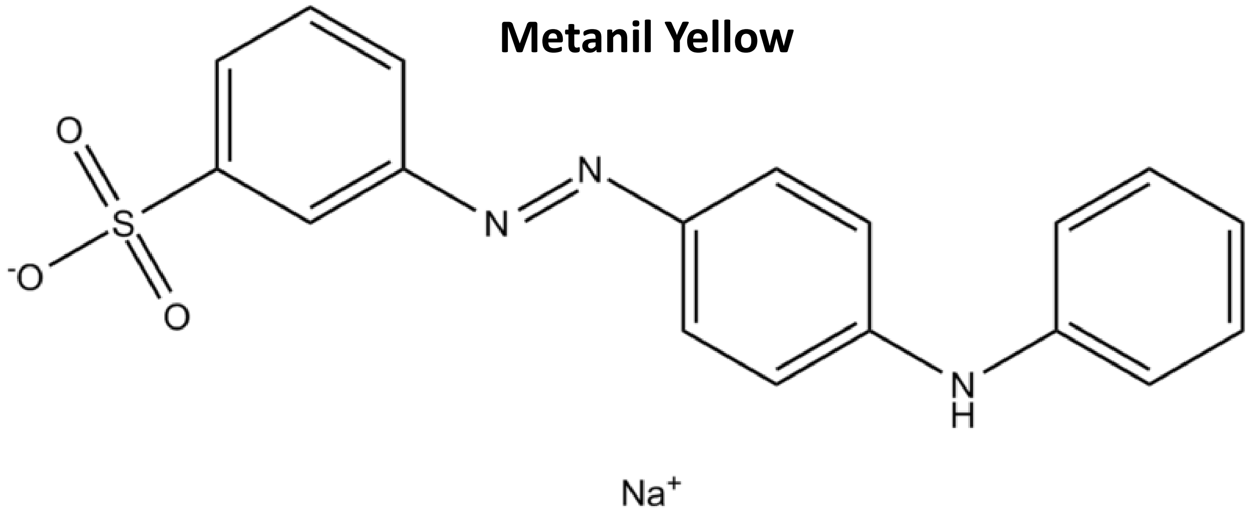
Sörengård, et al. (2020). Adsorption behavior of per-and polyfluoralkyl substances (PFASs) to 44 inorganic and organic sorbents and use of dyes as proxies for PFAS sorption. *Journal of Environmental Chemical Engineering*, *8*(3), 103744.

- Indigo carmine
- Metanil yellow
- Sulfonic acids like PFOS and PFHxS.
- Insensitive to pH changes typical of drinking water
- Similar weight and dimensions as some PFAS
- Downside: Chlorine reactivity.

Indigo Carmine

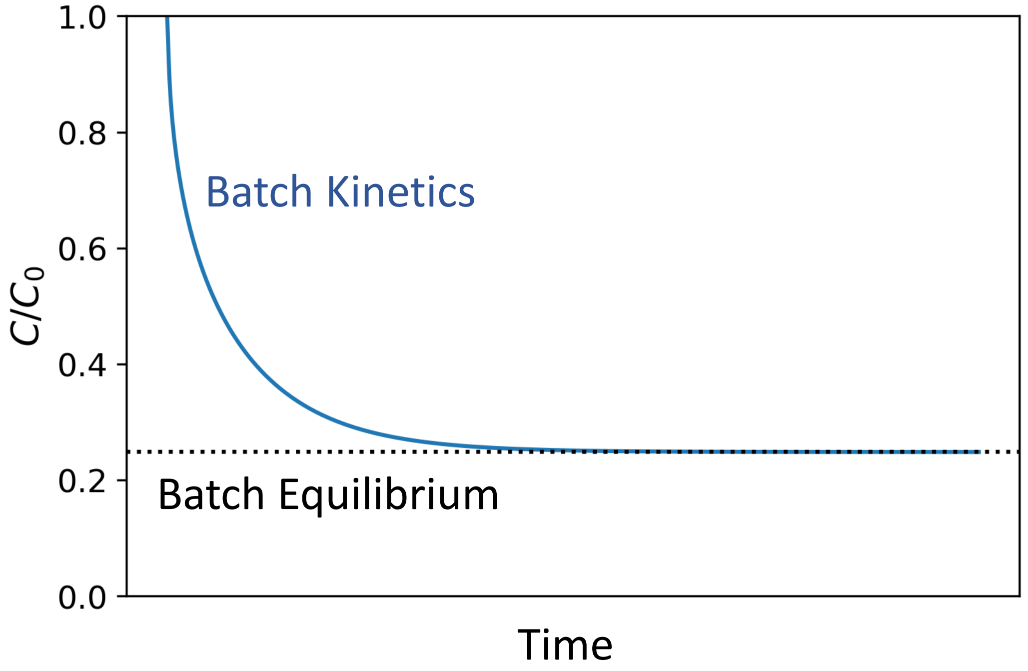


Metanil Yellow

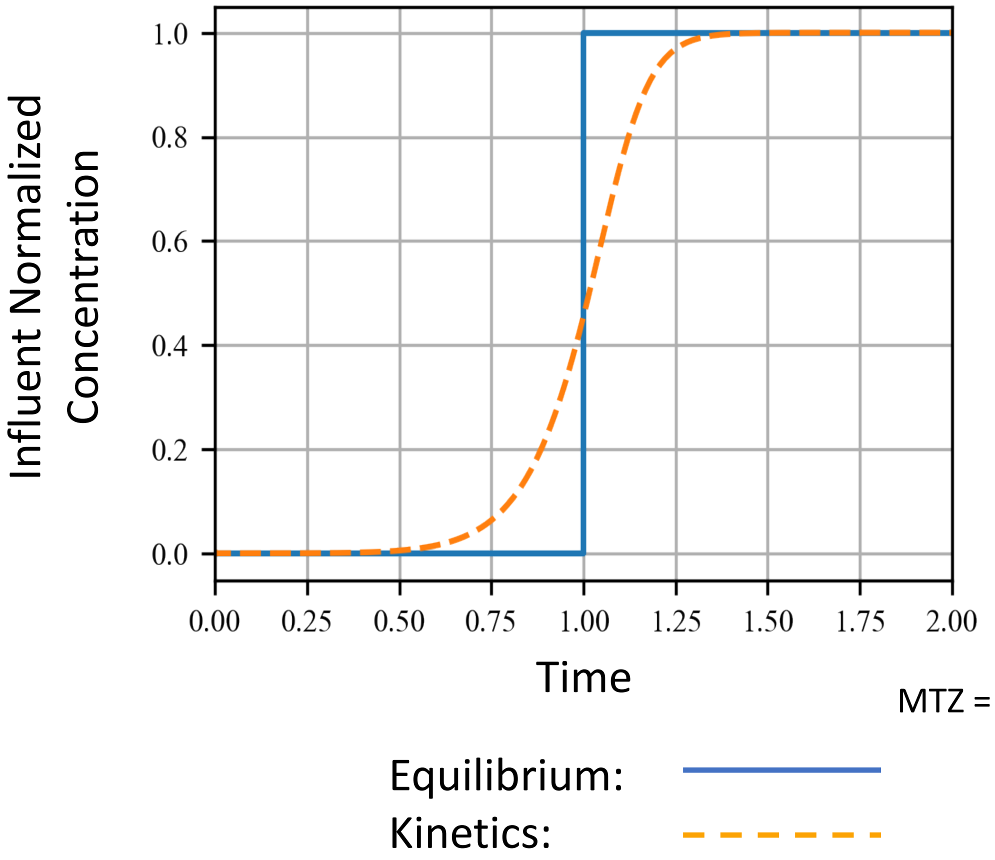


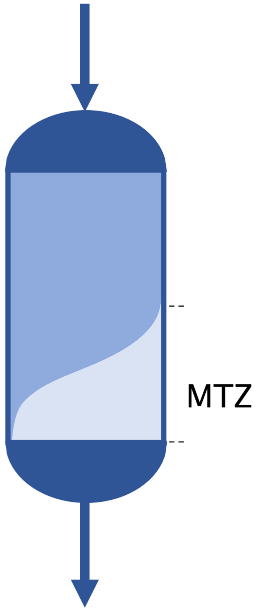
Kinetics and Equilibria

- How to tell if a dye is a good proxy for a given PFAS?
- Determine resin affinity (equilibrium)
- Measure how quickly adsorption happens (kinetics)



Column Breakthrough Curves





MTZ = Mass Transfer Zone

Approach

- Batch tests with resins, dyes, and salt.
- Matrix: Ultrapure water with sodium chloride and sodium bicarbonate.
- Measure dye concentrations with spectrophotometer.
- Determine equilibrium and kinetics.
  - Intraparticle diffusion and resin affinity measurements are transferrable to column models.
- Compare dye results to literature values for PFAS on same resins.

- Strong base, anion exchange
- Polystyrene-divinylbenzene
- Commonly marketed for PFAS treatment
- Chloride form
- Both gel-type and macroporous resins were investigated.

Anion Exchange Resin

Ion Exchange Equilibrium

- Ion exchange is a multi-component process.
- For ions to be adsorbed, other ions must desorb from resin.
- Contrast to single component isotherms commonly used in the adsorption literature.
  - Single component Langmuir
  - Freundlich

Apparent equilibrium constant

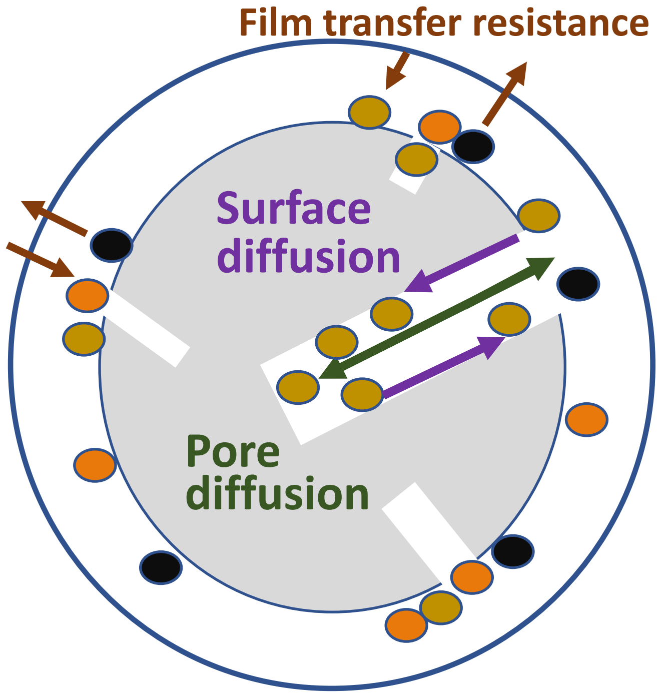
$$K_{BA} = \left(\frac{q_B}{C_B}\right)^{Z_A} \left(\frac{C_A}{q_A}\right)^{Z_B}$$

A, B: Ions being exchanged
q: resin phase concentration
C: liquid phase concentration
Z: ionic charge

Model specification: Smith, et al. (2023). Anion Exchange Resin and Inorganic Anion Parameter Determination for Model Validation and Evaluation of Unintended Consequences during PFAS Treatment. *ACS ES&T Water.*

Ion Exchange Kinetics

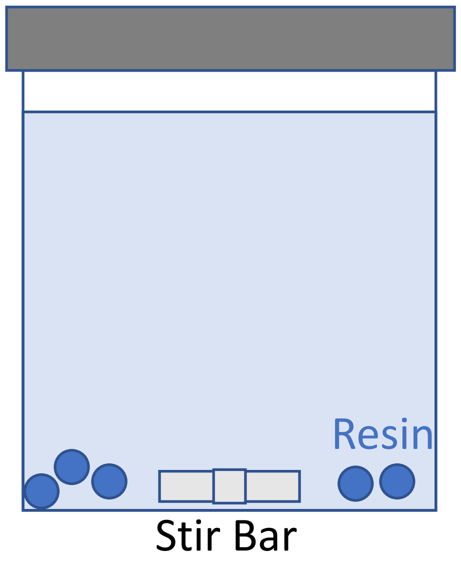
- Kinetics in ion exchange resins are controlled by diffusion processes.
  - Contrast to commonly applied pseudo-second order rate law, which assumes chemical reaction is rate limiting.
- Ions crossing from bulk liquid encounter film transfer resistance.
- Ions inside resins diffuse through the polymer matrix and pore spaces.
- For gel-type resins, and macroporous resins under certain conditions, pore diffusion can be ignored.
- Transport of ions is charge coupled.

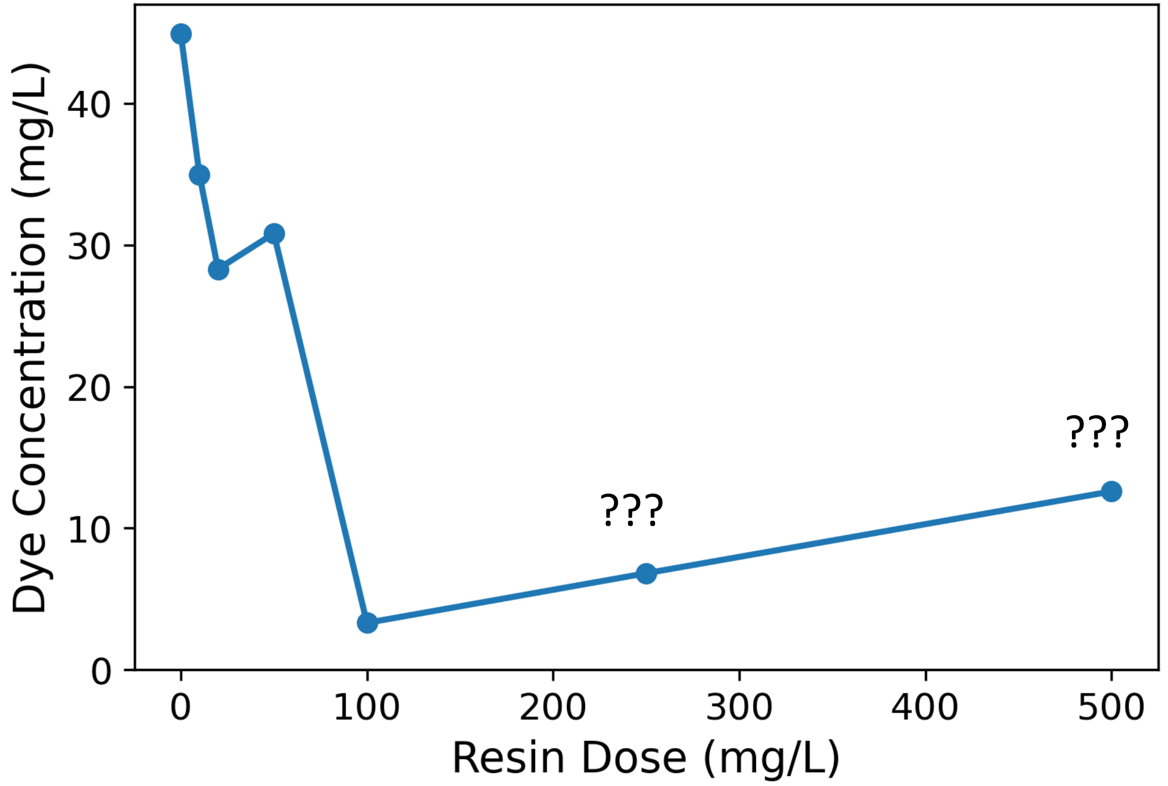


Model specification: Smith, et al. (2023). Anion Exchange Resin and Inorganic Anion Parameter Determination for Model Validation and Evaluation of Unintended Consequences during PFAS Treatment. *ACS ES&T Water.*

Initial Resin Dose Screening

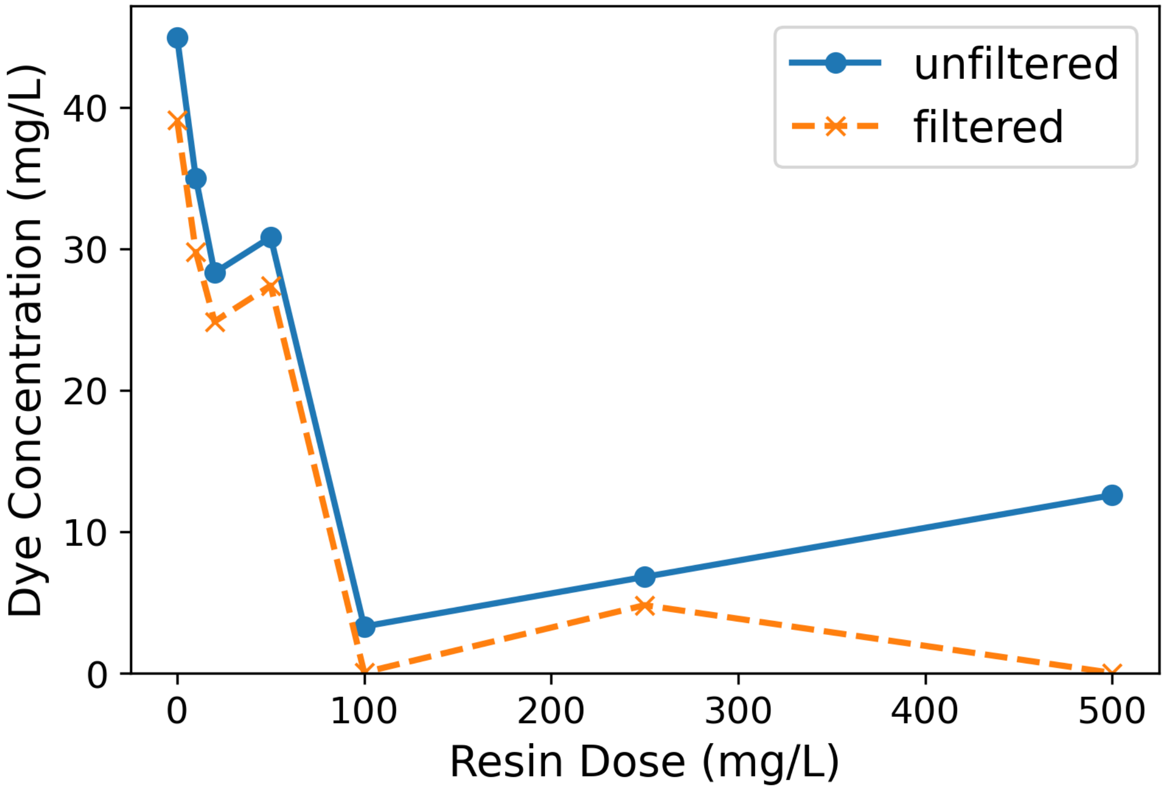
- Try several resin doses
- Include background salts
- Use rough estimate of affinity and kinetics to design next tests
- Unexpected result!





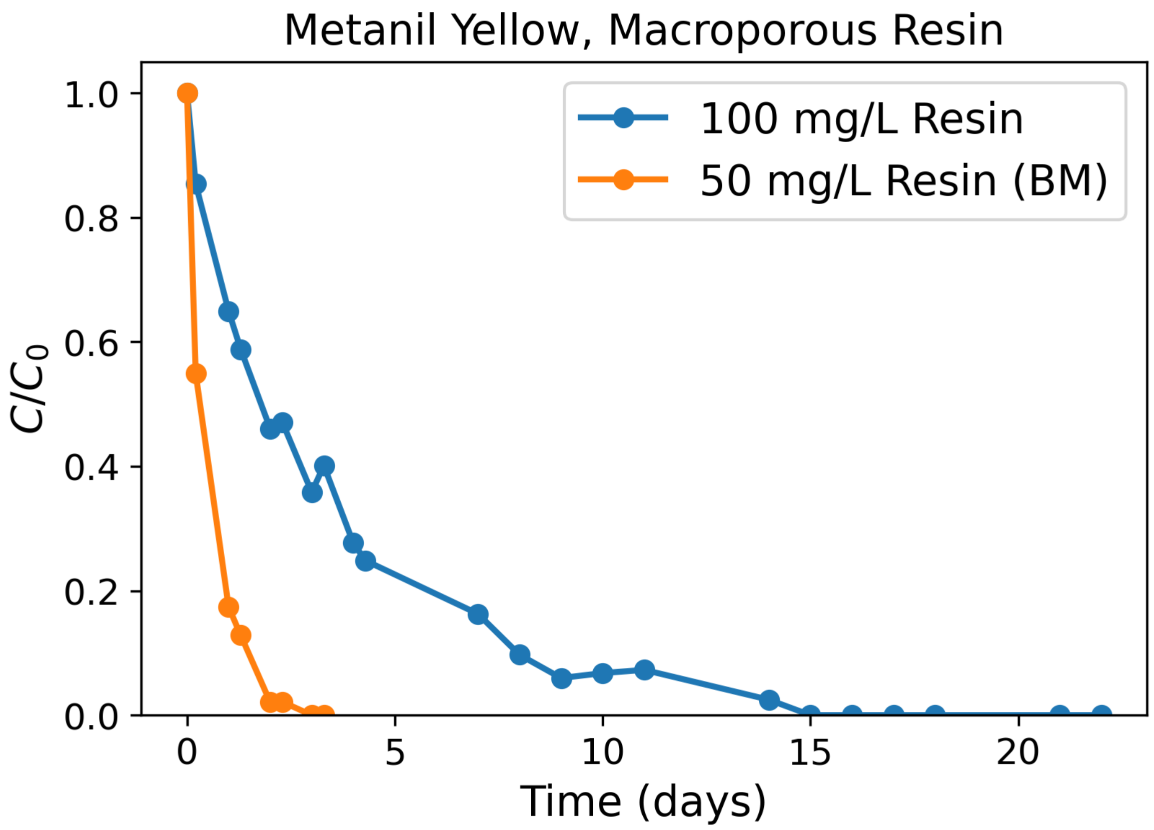
Stir Bar Issue

- Solutions looked cloudy
- Physical filtering solution reduced the issue.
- Fine particles were absorbing/scattering light.
- **Issue:** Stir bar pulverized resins.
- **Solution:** Use rotators instead.



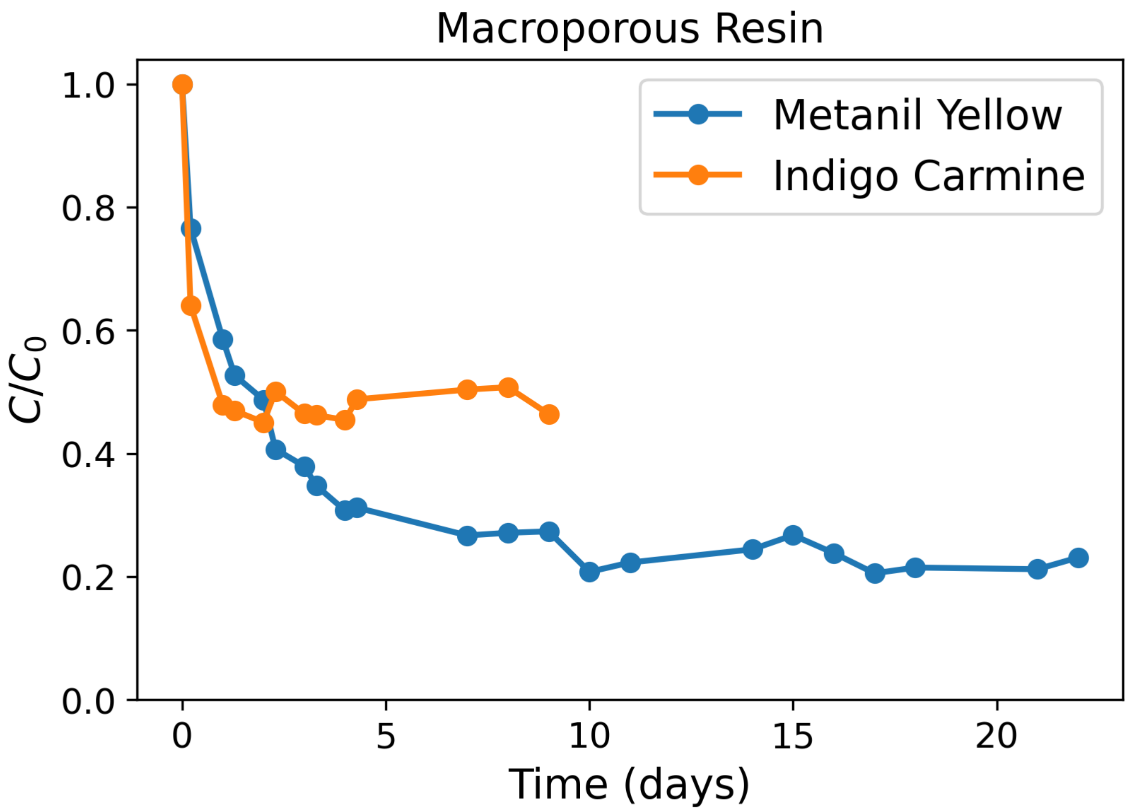
Kinetic Issues: Grinding

- Full size resins have slow kinetics
- Weeks to equilibrium for resin doses less than 250 mg/L.
- Small size resins allow for rapid experiments.
- Design full size experiments to answer questions more effectively
- Resins were ball-milled (BM) and sieved to 100x200 mesh size fraction.
  - Full size: 0.75 mm diameter
  - BM: 0.11 mm diameter
- **Next problem**: finding a resin dose that doesn't drop dyes to non-detect.



Equilibrium Measurements

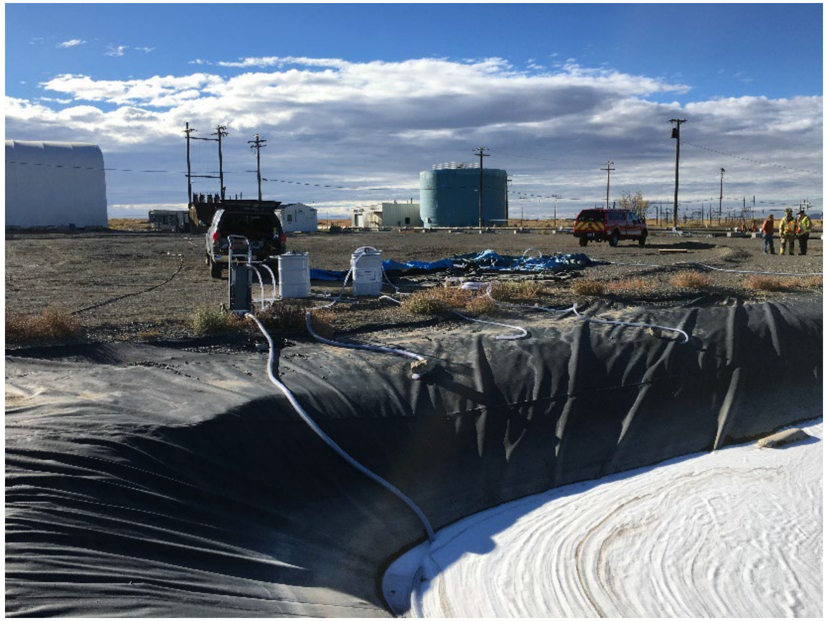
- A resin dose of 25 mg/L resulted in measurable equilibrium concentrations.
- C_0 dyes ~18 mg/L
- After adjusting for molecular weight and valence, dye uptake (both dyes) was within 5% of resin exchange capacity despite competition from chloride (88 mg/L).
- Dye affinities for resins are high. Likely somewhere between PFHxA and PFOA.[1]
- Equilibrium results seem promising for using dyes as PFAS proxies on these resins.
- Analysis and comparison of kinetics with PFAS experiments are still underway.



1: Fang, et al. (2021). Removal of per-and polyfluoroalkyl substances (PFASs) in aqueous film-forming foam (AFFF) using ion-exchange and nonionic resins. *ACS ES&T*, 55(8), 5001-5011.

Sometimes PFAS Behave Strangely

- Non-exchange sorption occurs at high PFAS concentrations.[1]
  - Micelle formation or co-ion invasion?
  - Less important for drinking water, but physically and practically interesting
  - Might be relevant for other PFAS contamination scenarios
- Max sorption of PFOS is less than ion exchange capacity on some gel-type resins.[2]

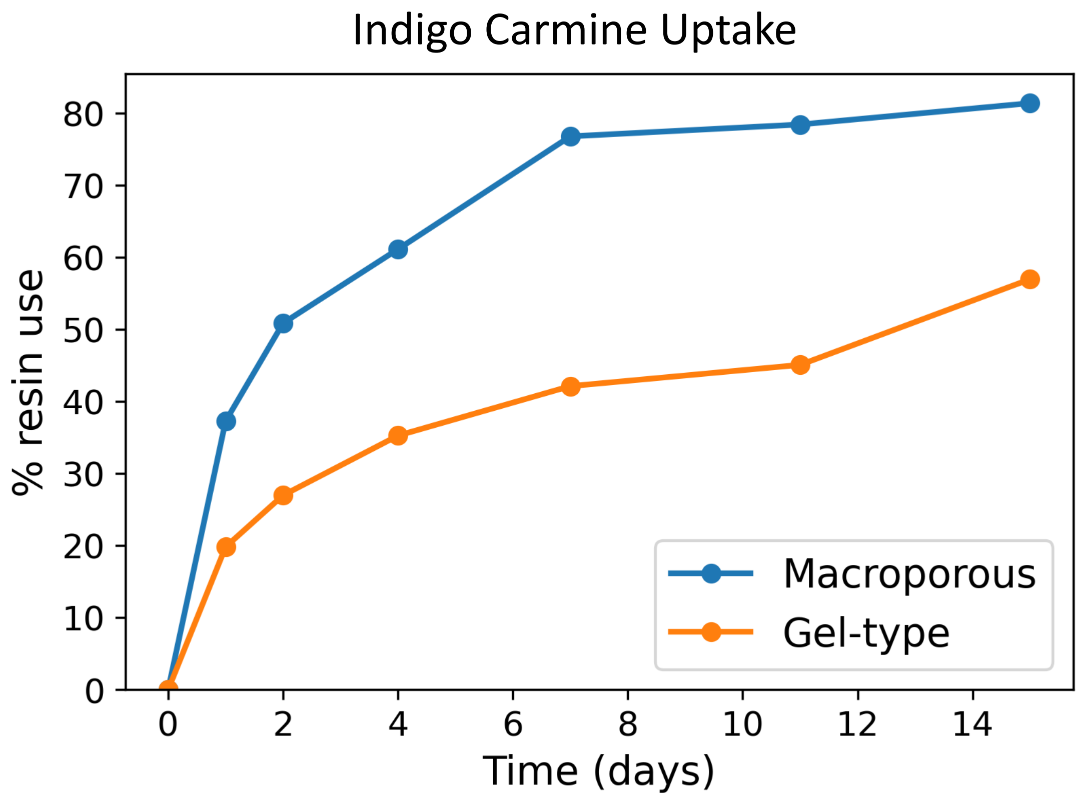


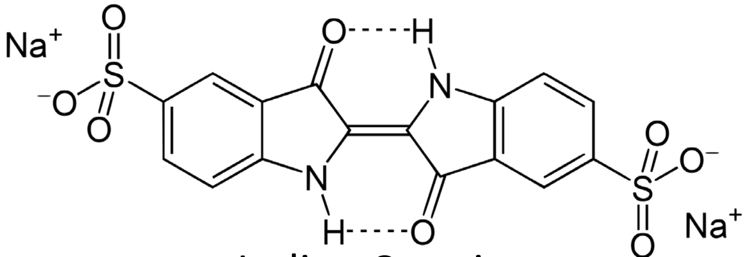
Onsite treatment of impounded AFFF foam

1: Zaggia, et al. (2016) Use of strong anion exchange resins for the removal of perfluoroalkylated substances from contaminated drinking water in batch and continuous pilot plants, *Water Research,* 91, 137-146
2: Fang, et al. (2021). Removal of per-and polyfluoroalkyl substances (PFASs) in aqueous film-forming foam (AFFF) using ion-exchange and nonionic resins. *ACS ES&T*, 55(8), 5001-5011.

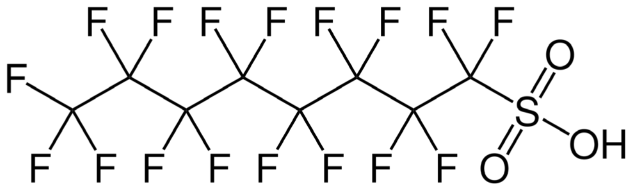
Aside: A PFOS Question

- Fang et al. reports low PFOS utilization on gel type resins.
  - 4-17%
- Why does that happen?
- Can dyes answer that question?
- Dyes have similar dimensions and same acid group as PFOS.
- Ongoing kinetic experiments on full size resins show higher resin utilization than PFOS.
- Seems to suggest against a simple size exclusion explanation.





Indigo Carmine



PFOS

Conclusions

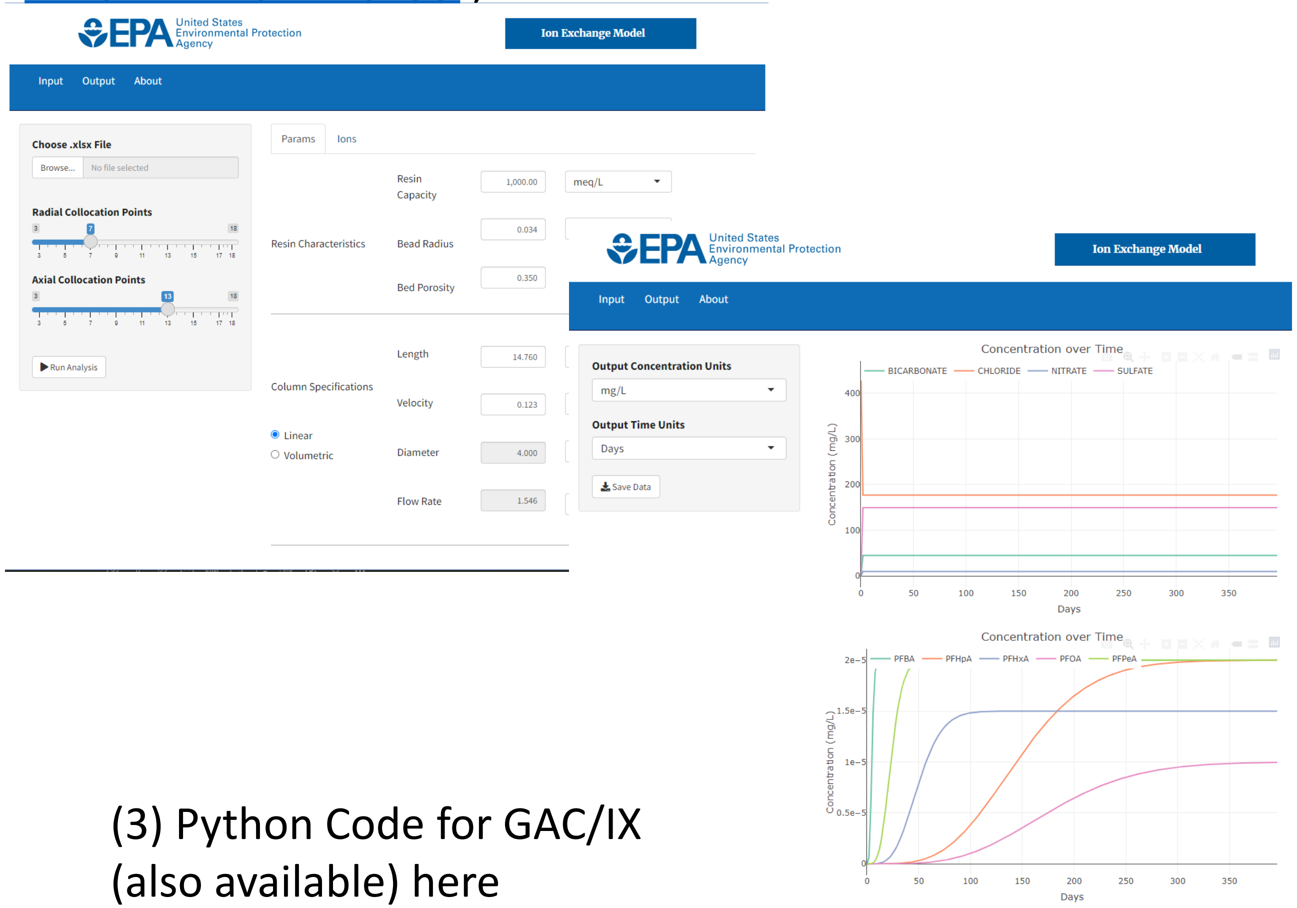
- Summary:
  - Equilibrium batch studies suggest metanil yellow and indigo carmine may be suitable proxies for some PFAS on polystyrene, strong-base anion exchange resins that are selective for PFAS.
  - Dyes may provide an inexpensive and rapid method to screen or optimize experiments and treatment systems.
  - Experiments with dye proxies can shed light on fundamental questions about adsorption on ion exchange resins.

- Future work
  - Measure dye resin affinity precisely by varying salt concentrations or other isotherm conditions.
  - Compare kinetics of dyes and PFAS in batch experiments.
  - Run column experiments with dye experiments and link results to batch results.

Model Development and Availability

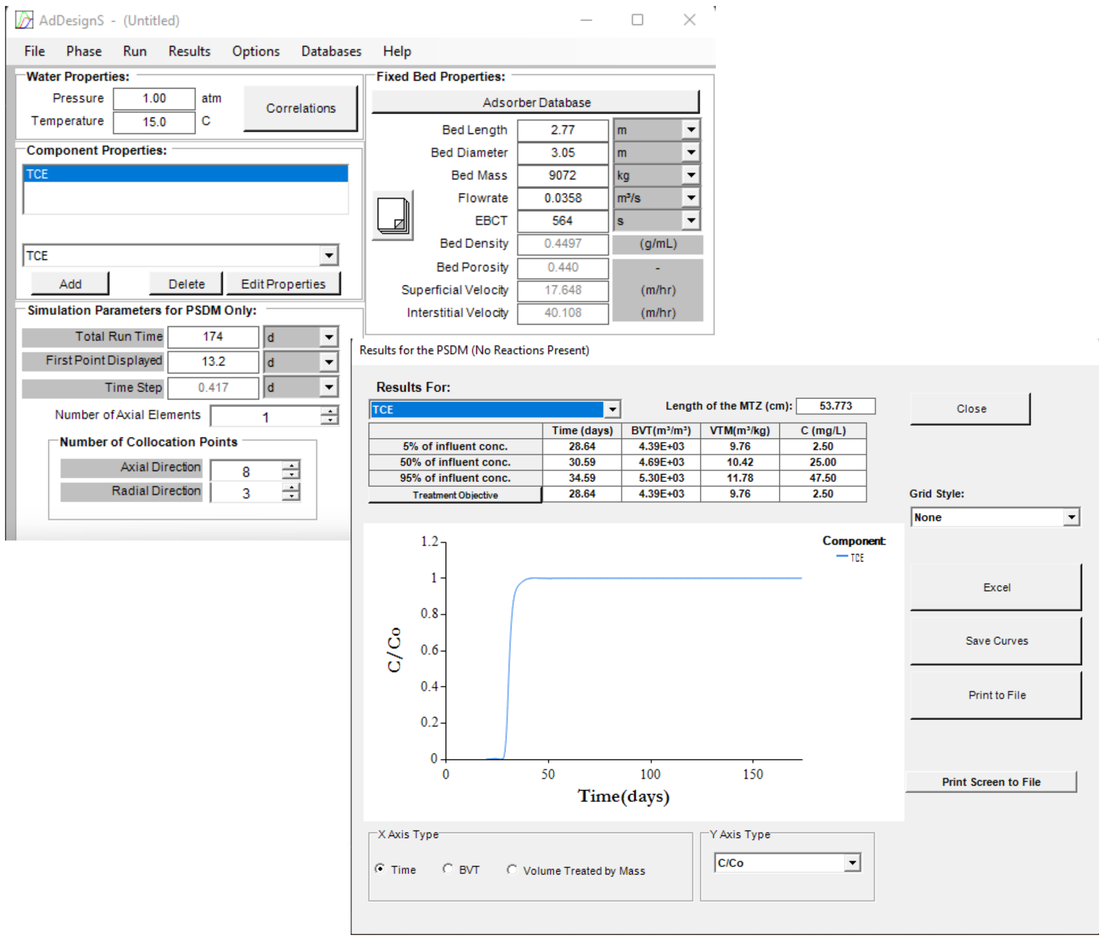
(1) Ion Exchange (IX) Column Model

(https://github.com/USEPA/Water_Treatment_Models/tree/master/ShinyApp)



(2) GAC – AdDesignS

https://github.com/USEPA/Environmental-Technologies-Design-Option-Tool/releases/download/1.0.50/AdDesignS_updated.zip



	Time (days)	BVT(m³/m³)	VTM(m³/kg)	C (mg/L)
5% of influent conc.	28.64	4.39E+03	9.76	2.50
50% of influent conc.	30.59	4.69E+03	10.42	25.00
95% of influent conc.	34.59	5.30E+03	11.78	47.50
Treatment Objective	28.64	4.39E+03	9.76	2.50

(3) Python Code for GAC/IX (also available) here

https://github.com/USEPA/Water_Treatment_Models

EPA's Drinking Water Cost Models

- Adsorptive media
- **Anion exchange***
- Biological treatment*
- Cation exchange
- **GAC***
- Greensand filtration
- Microfiltration / ultrafiltration
- Multi-stage bubble aeration*

- Non-treatment
- Packed tower aeration
- **POU/POE#**
- **Reverse Osmosis / Nanofiltration**
- UV disinfection
- UV Advanced Oxidation

***Search: EPA WBS** https://www.epa.gov/sdwa/drinking-water-treatment-technology-unit-cost-models

 # For POU/POE search: EPA small system compliance help
http://water.epa.gov/type/drink/pws/smallsystems/compliancehelp.cfm

Questions?

Dyes may provide an inexpensive and rapid method to screen or optimize experiments and treatment systems for PFAS. Experiments with dye proxies can shed light on fundamental questions about adsorption on ion exchange resins.

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https://github.com/USEPA/Environmental-Technologies-Design-Option-Tool
https://github.com/USEPA/Water_Treatment_Models
https://www.epa.gov/sdwa/drinking-water-treatment-technology-unit-cost-models