Treatment of environmentally relevant PFAS concentrations with ion exchange resins

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TEMPLE UNIVERSITY

Science of PFAS
April 5, 2022

Project contributors

- Ex Situ Treatment of PFAS Contaminated Groundwater Using Ion Exchange with Regeneration (ER18-1027)

Drs. Mark E. Fuller, Paul B. Hatzinger
Aptim Federal Services (formerly CB&I)
Expertise: In situ and ex situ remediation of environmental contaminants; electrochemical degradation of PFASs

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Expertise: PFAS analytical methods; sonochemical degradation of PFASs and other compounds

Mr. Francis Boodoo
Purolite Corporation
Expertise: IX resin chemistry, development, and testing

APTIM

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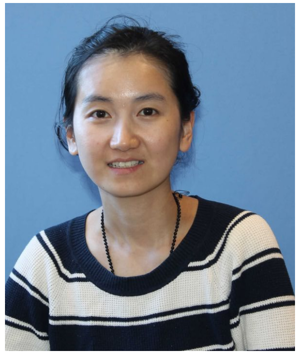

Yi Zhang

Yaseen Al-qaraghuli

Scope: evaluate 5 reins and AC performance; regeneration

General overview

Strengths
- Mature
- Potential improved performance
- Rapid process
- Long life
- Potential regeneration

Weaknesses
- Few full-scale PFAS projects
- Expense
- Pre-treatment may be needed
- Competition from other ions
- Regenerant management

https://www.purolite.com/

Resin essentials

- Focusing on anion exchange resins for treatment of “legacy” anion PFAS
- Polymer chemistry and matrix
  - Affects hydrophobicity (as well as stability)
  - Macroporous – more open structure, limited steric effects => faster kinetics
  - Gel – more stable, more capacity, more steric effects => slower kinetics
- Base strength
  - Strong base resins – can work at a variety of pH values
  - Weak base resins – need to be partially protonated (e.g. pH <~ 5.5)

Removal process

Exchange of solid associated ion ($\equiv B^-$; Cl^-) with aqueous ion ($PFAS^-$), resulting in swap ($\equiv A^-$ and aqueous ion B^-)

$$\equiv B^- + PFAS^- \rightarrow \equiv PFAS^- + B^-$$


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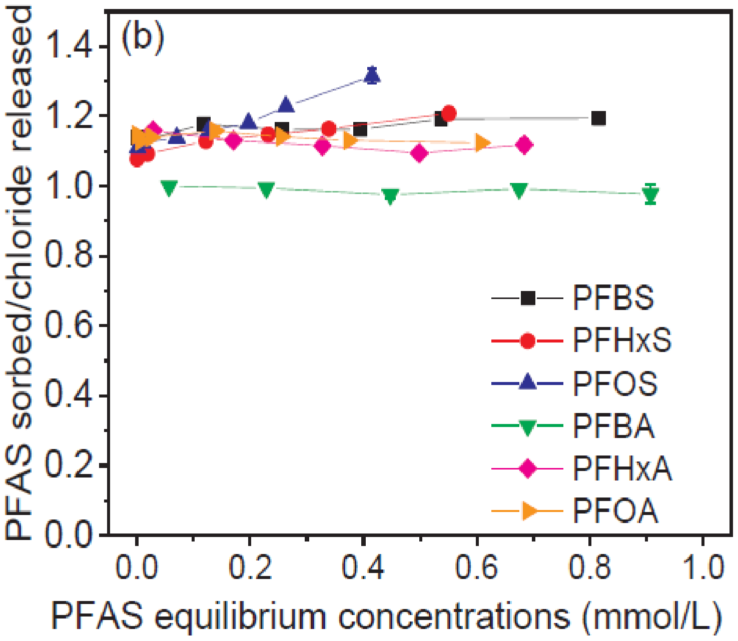
Competitive adsorption of perfluoroalkyl substances on anion exchange resins in simulated AFFF-impacted groundwater

Ayiguli Maimaiti, Shubo Deng*, Pingping Meng, Wei Wang, Bin Wang, Jun Huang, Yujue Wang, Gang Yu

- But… can also have hydrophobic interactions impact
  - Literature generally suggests that both ion exchange and hydrophobic interactions affect PFAS removal, particularly for longer chain length compounds
  - Polymer hydrophobicity could be a factor
  - PFAS removal > Cl^- release (Deng, 2010; Maimaiti, 2016)



Our Goals

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- Determine removal capacity at environmentally relevant [PFAS]
- Compare performance to activated carbon
- Evaluate multi-cycle resin regeneration (batch system)
- Compare batch results to flow through regeneration (column) system

Overarching project approach

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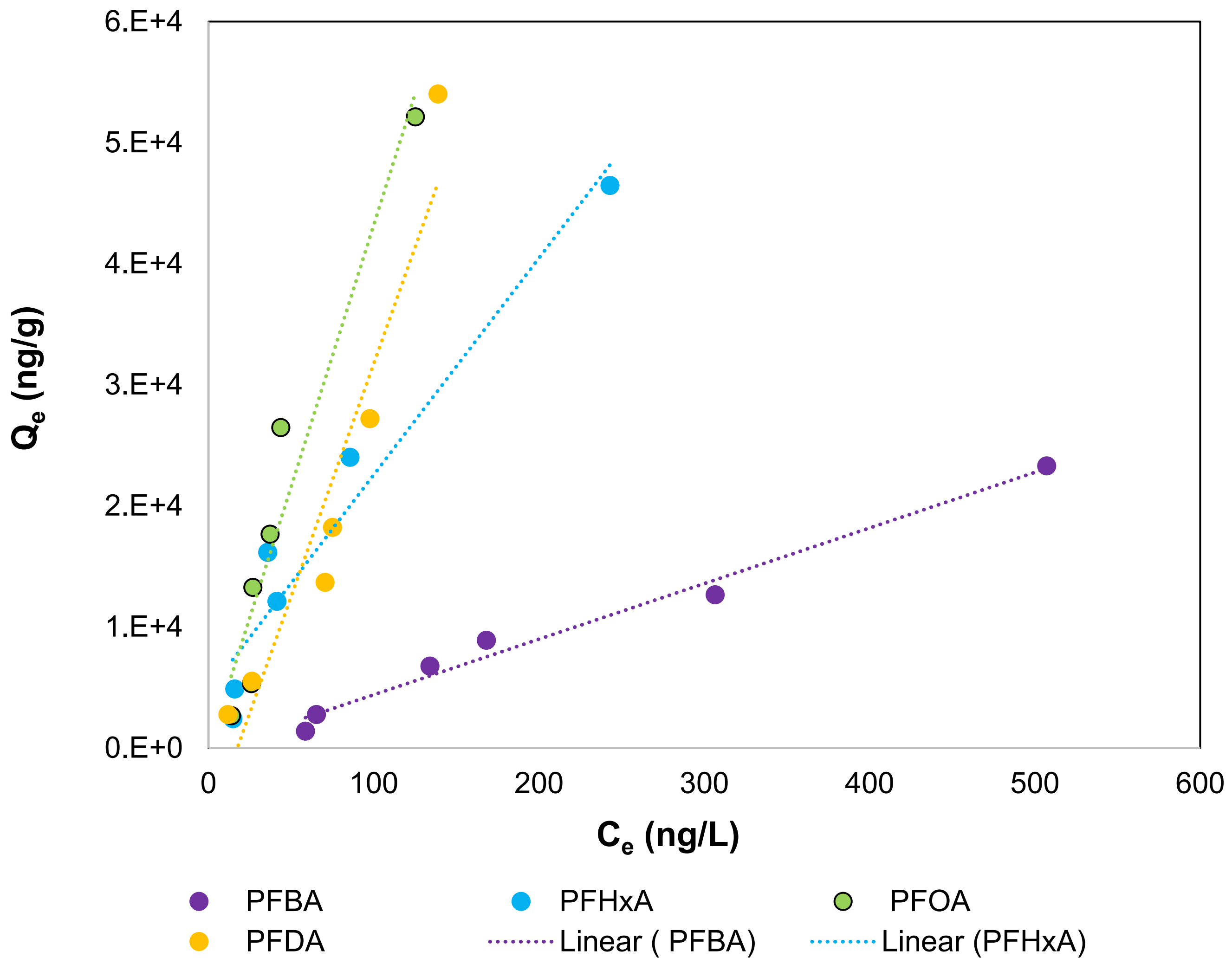
- 6 resins from Purolite:
  - 4 strong base resins/2 weak base resins
  - Range of expected regenerability
  - Analytical QA/QC issues with one of the strong base resins
- Use Calgon F400 as reference activated carbon
- Solution: artificial groundwater with initial [PFAS] = 10 nM
  - Generally include a suite of 14 PFAS
- Batch test: 50 mL solution with variable media
  - 5 – 100 mg
  - Measure aqueous concentration (SPE); calculate solid associated concentration

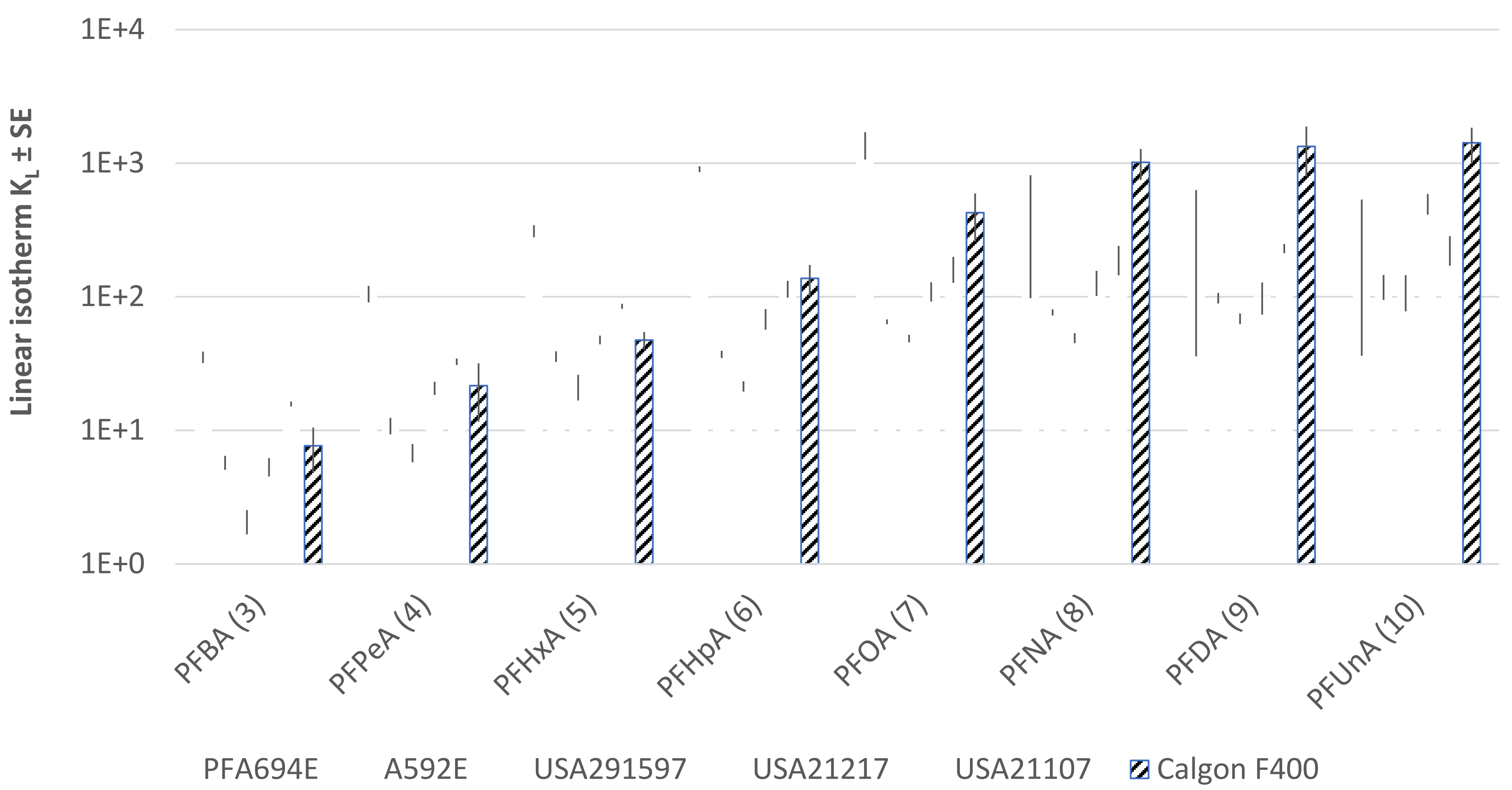
Batch isotherm - linearity

- Batch isotherm
  - Determine concentration effects
  - Compare capacity among PFAS
  - Compare capacity among resins

- Isotherms are **linear** at low concentrations!
  - Use this to determine K_L
  - Likely not true at higher [PFAS]

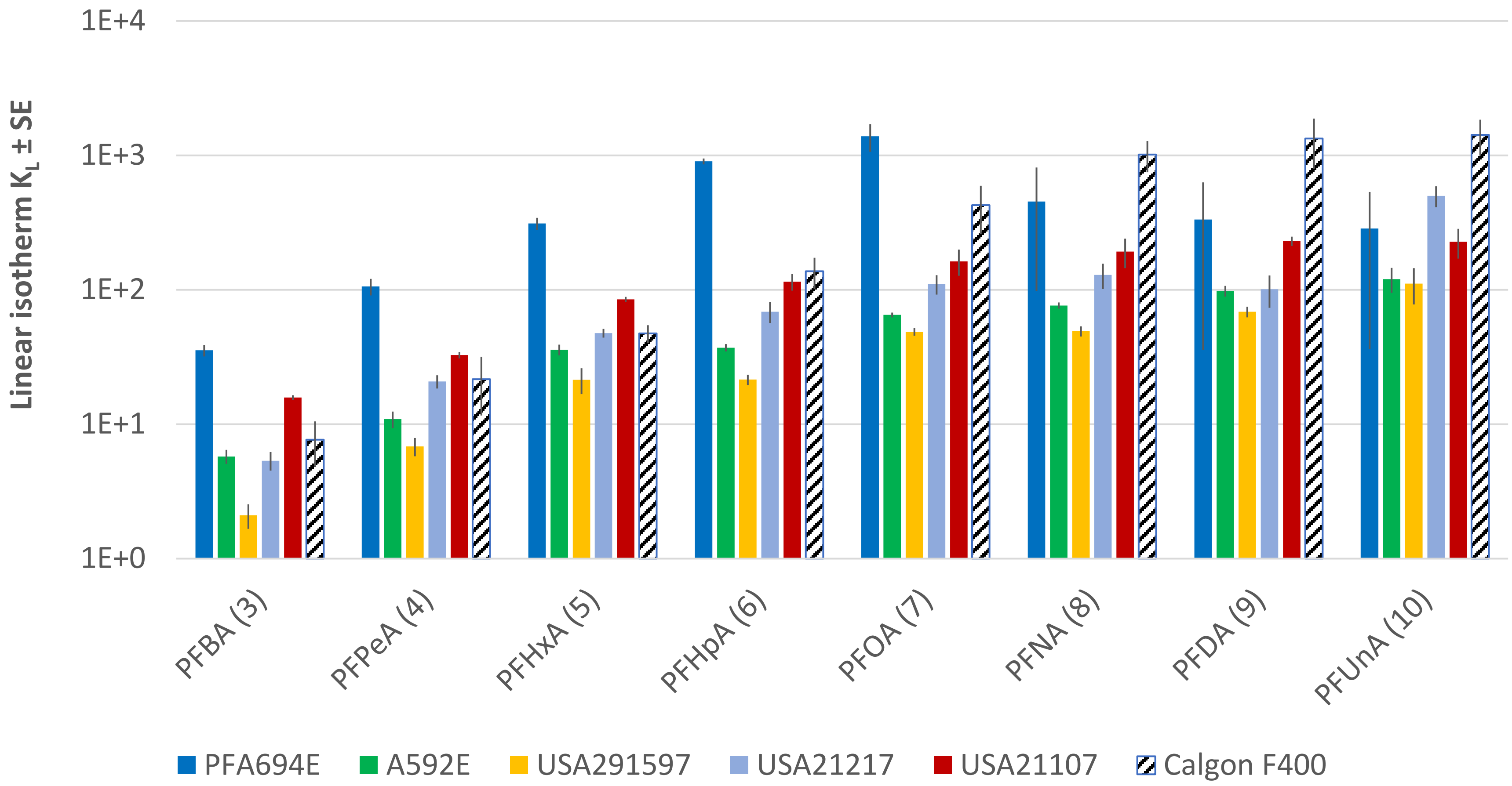


Batch isotherm – PFAS and resin effects



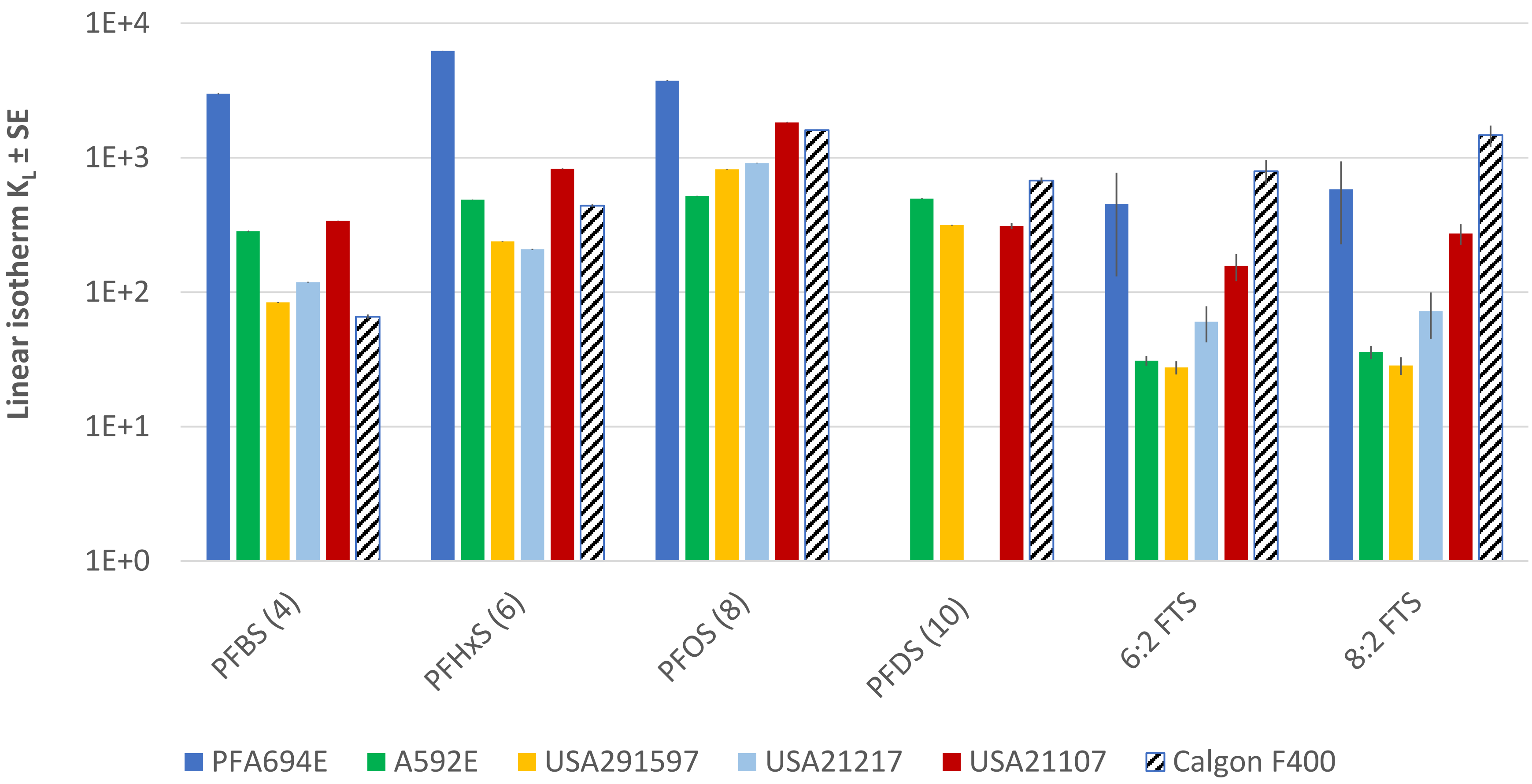
- For PFCAs, greater capacity for longer chain length

Batch isotherm – PFAS and resin effects



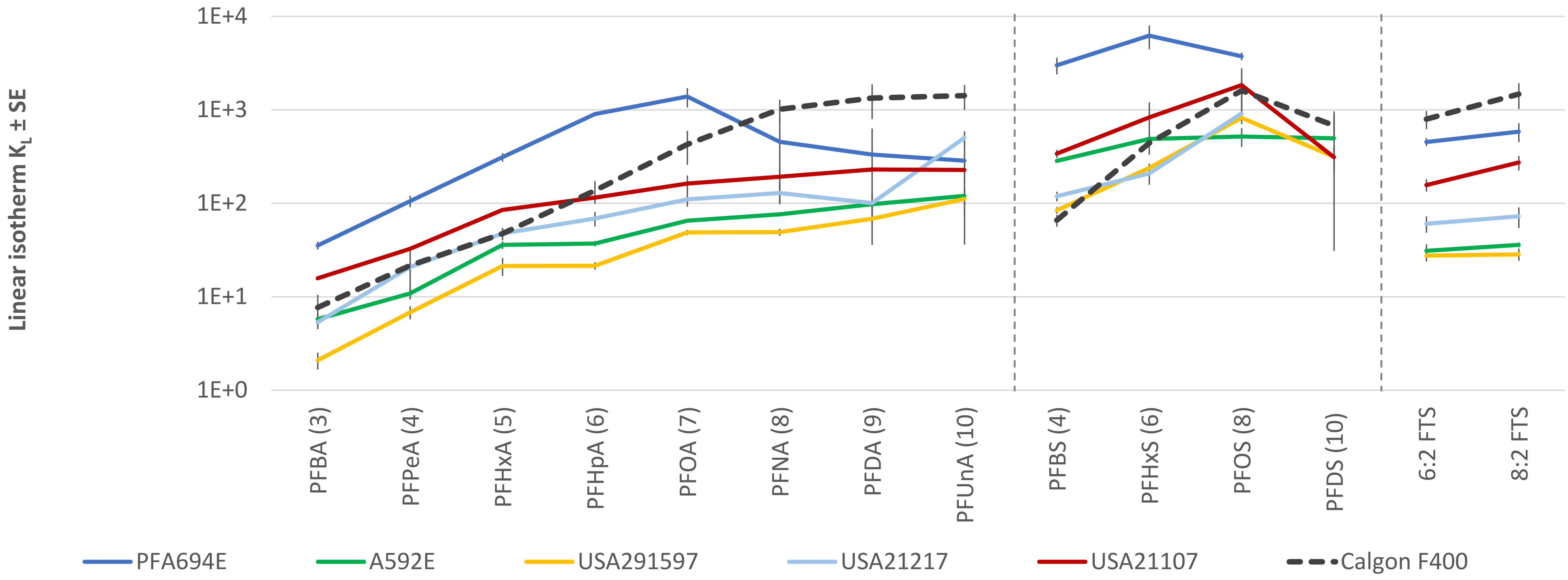
- For PFCAs, greater capacity for longer chain length
- Generally PFA692E > USA21107 ~ AC > others; reverse for longest chain length

Batch isotherm – PFAS and resin effects



- Fewer chain length effects for PFSAs and FTS
- Generally PFA692E > USA21107 ~ AC > others

Batch isotherm – resin effects

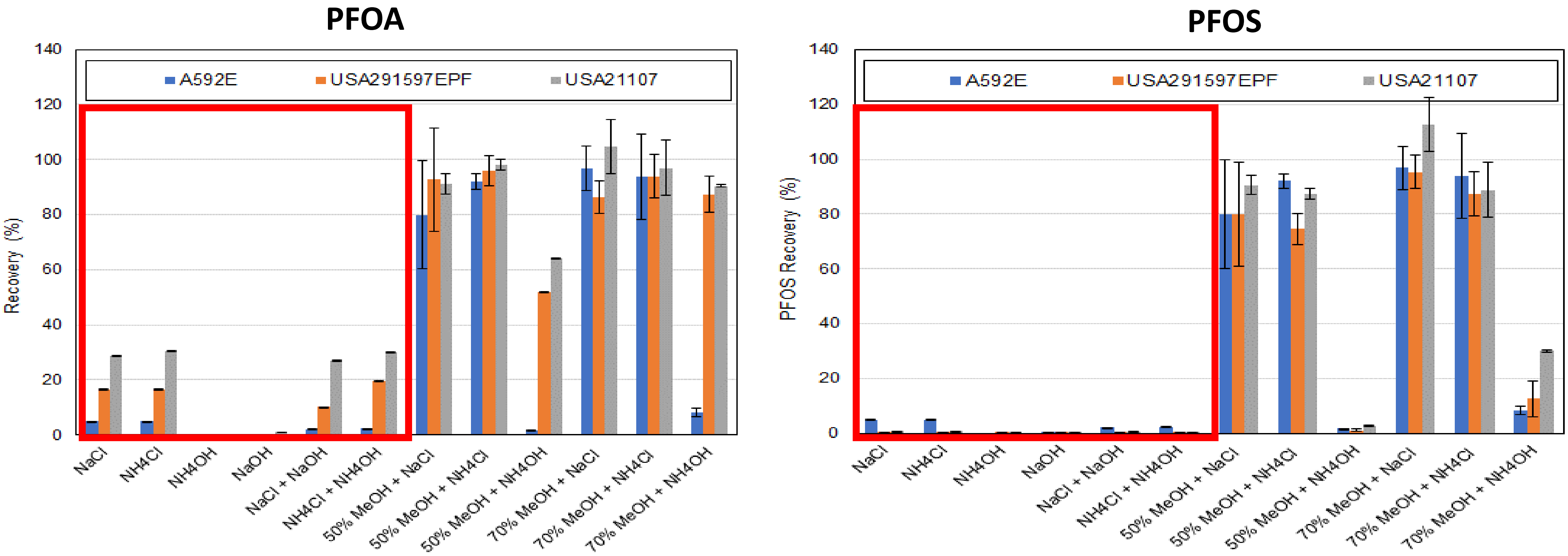


- PFA694E (strong base) and USA21107 (weak) outperform AC for shorter chain lengths

Regeneration testing

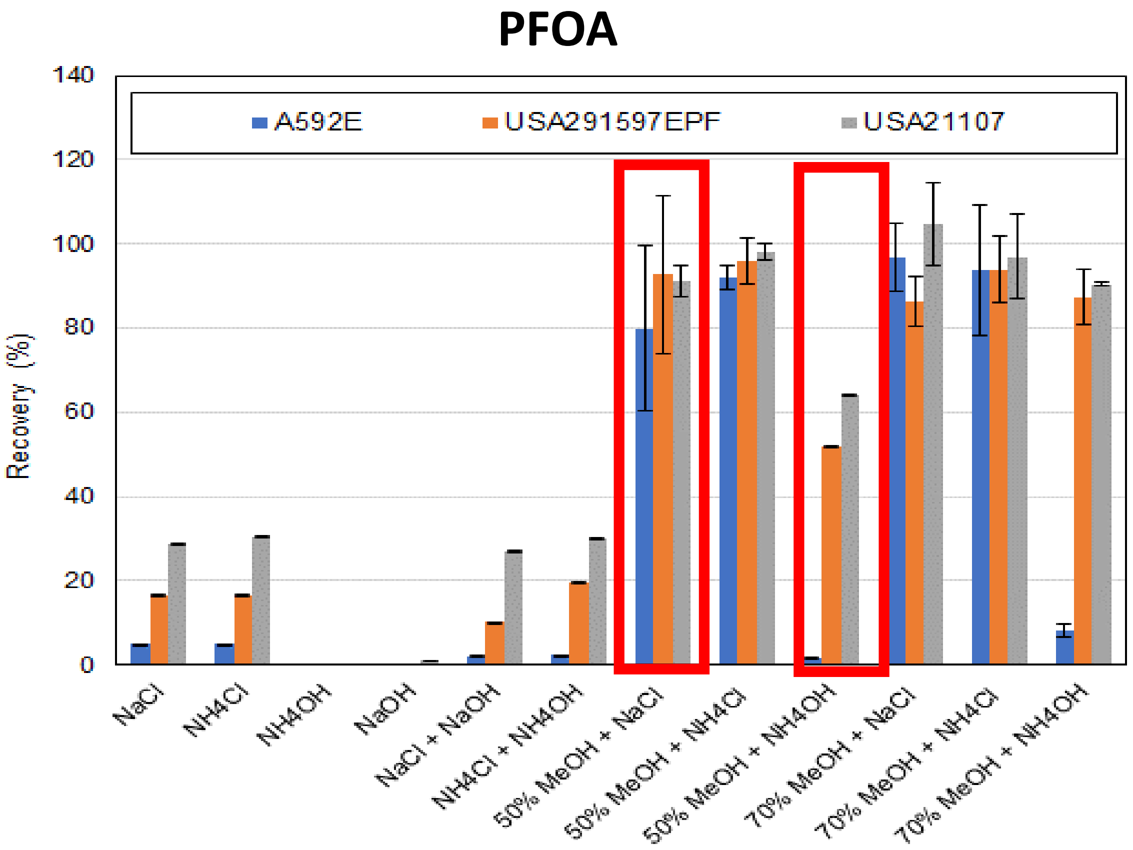
- Batch systems to load PFAS -> batch to test regeneration
  - Loading followed isotherm approach
- Aqueous brine regenerants (6 salts @ 0.17 M; equiv 1% NaCl)
- 50% methanol regenerants (3 salts @ 0.17 M; equiv 1% NaCl)
- 70% methanol regenerants (3 salts @ 0.17 M; equiv 1% NaCl)
- For select regenerants, tested multiple cycles

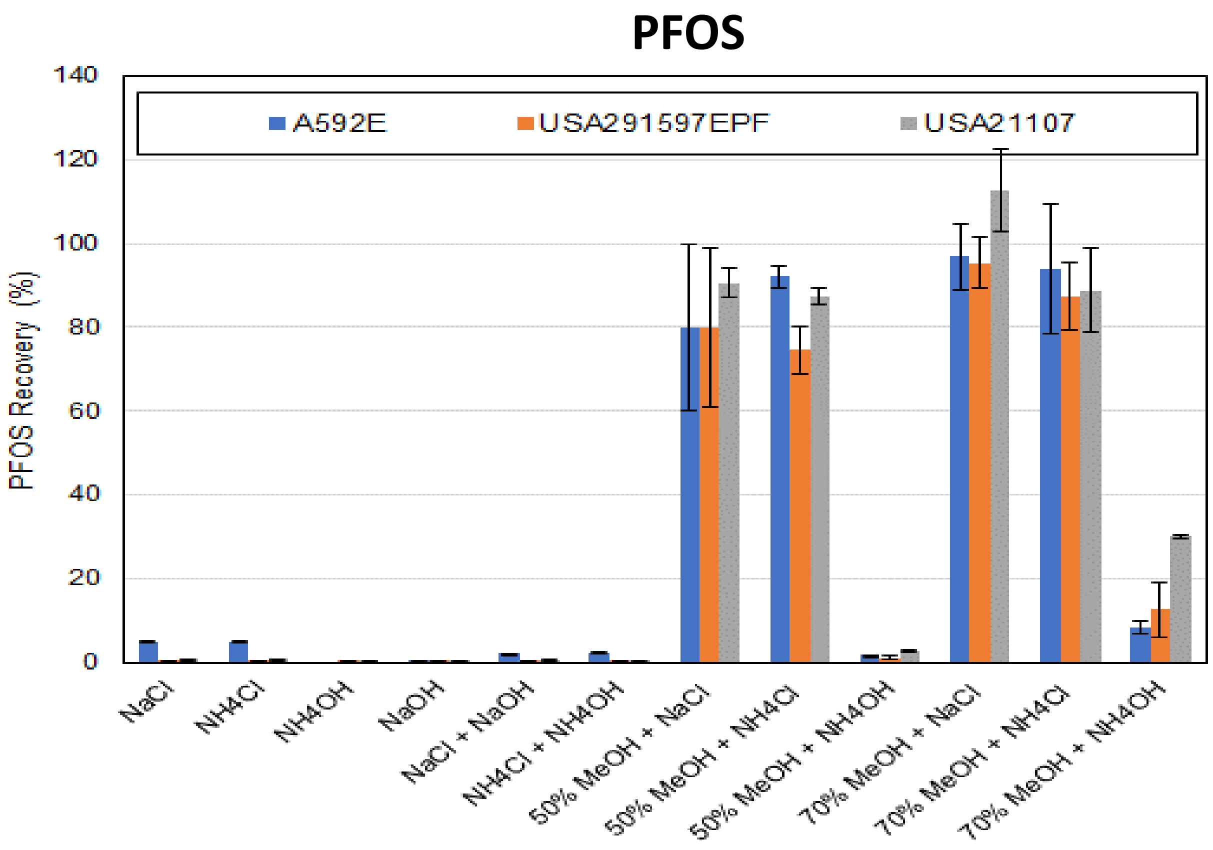
Batch regeneration



- **Aqueous regenerants performed OK for PFCA, but poorly with PFSA**

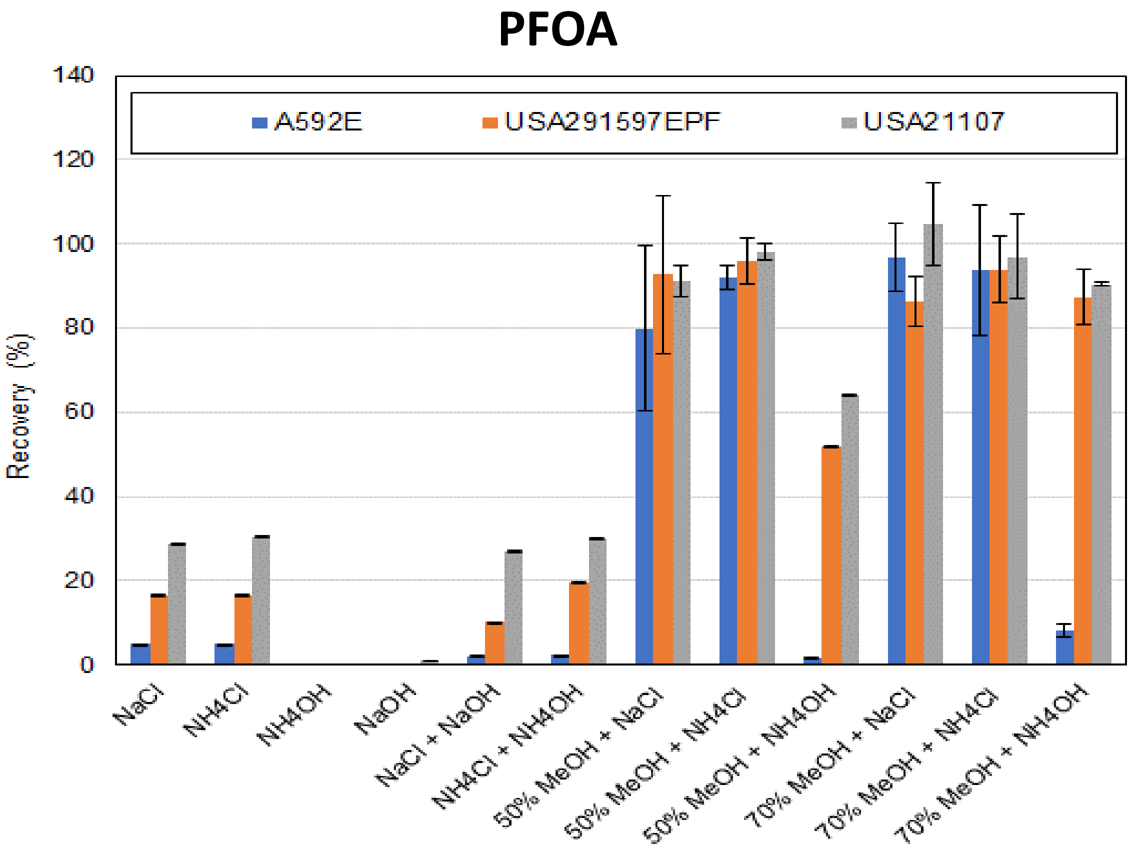
Batch regeneration

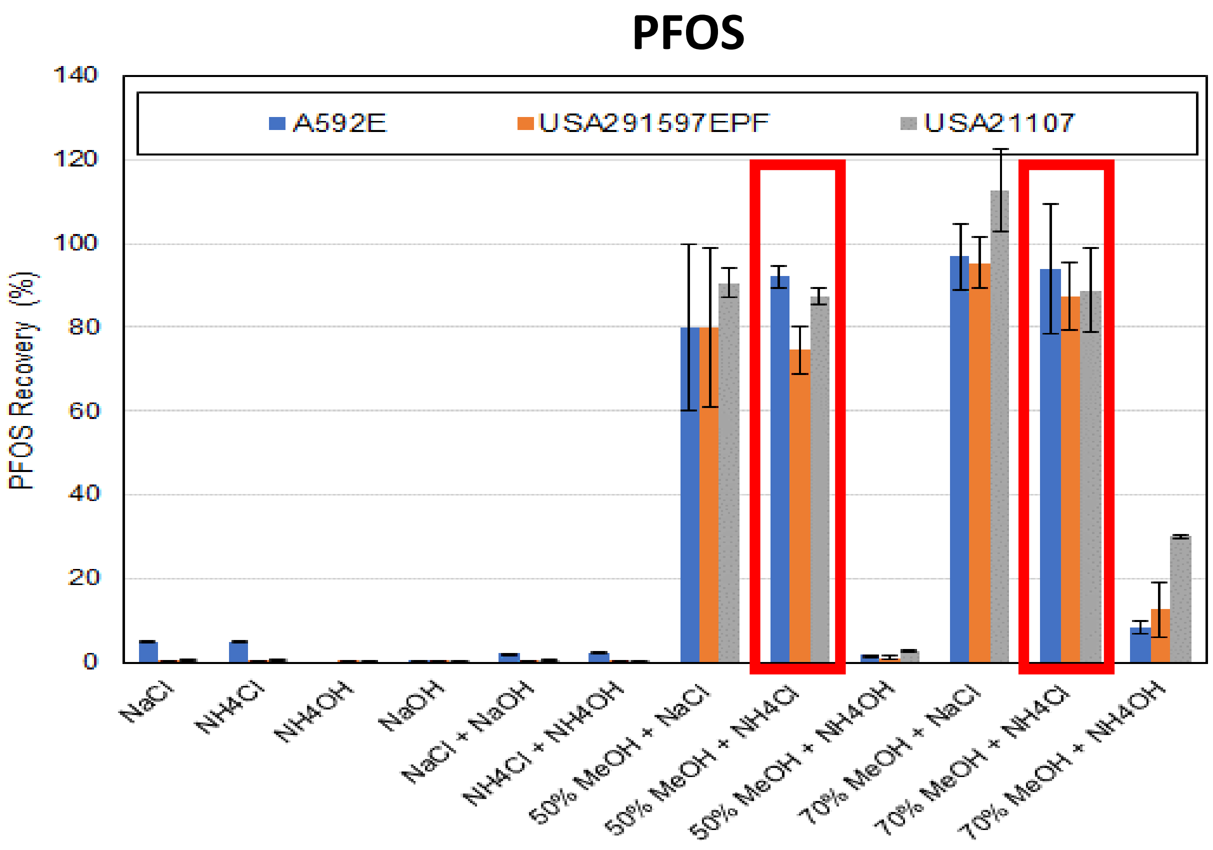




- **Aqueous regenerants performed OK for PFCA, but poorly with PFSA**
- **Chloride a better exchange anion than hydroxide; no clear benefit of NH_4-based salts**

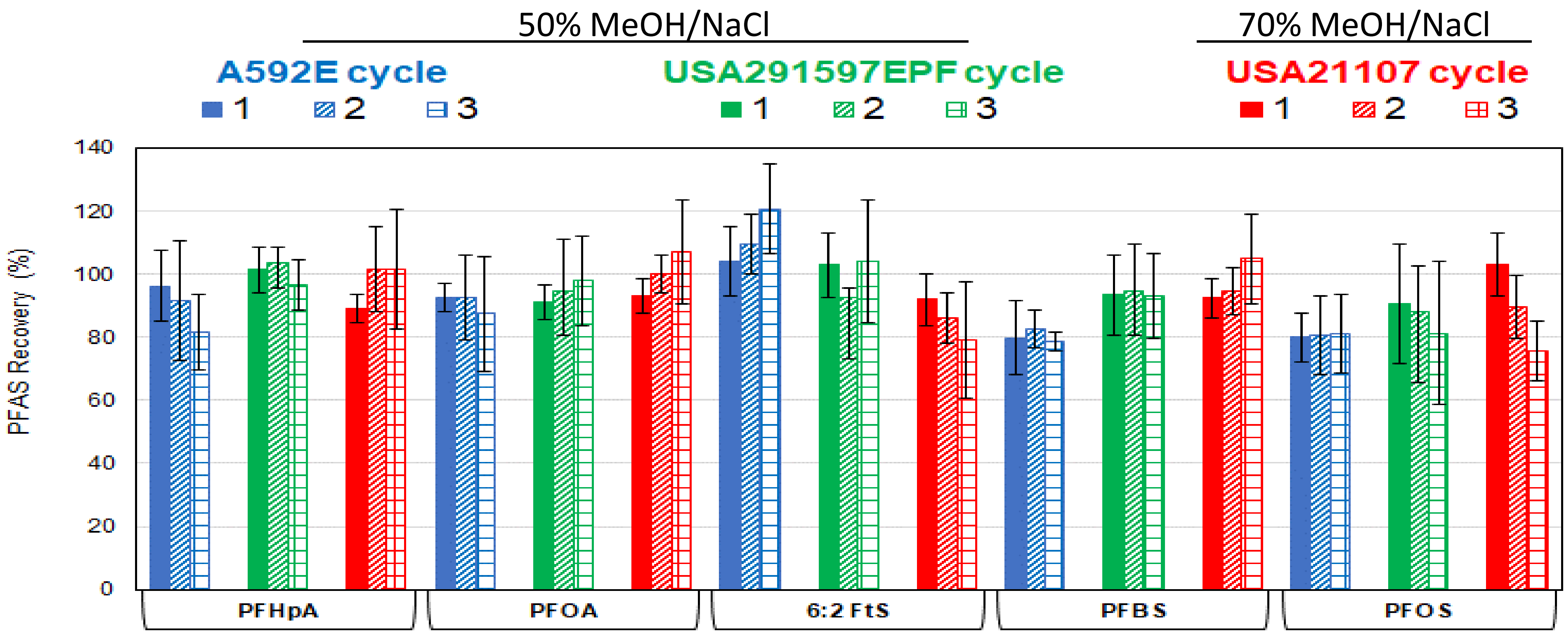
Batch regeneration





- **Aqueous regenerants performed OK for PFCA, but poorly with PFSA**
- **Chloride a better exchange anion than hydroxide; no clear benefit of NH_4-based salts**
- **50% MeOH and 70% MeOH generally similar, except USA21107**

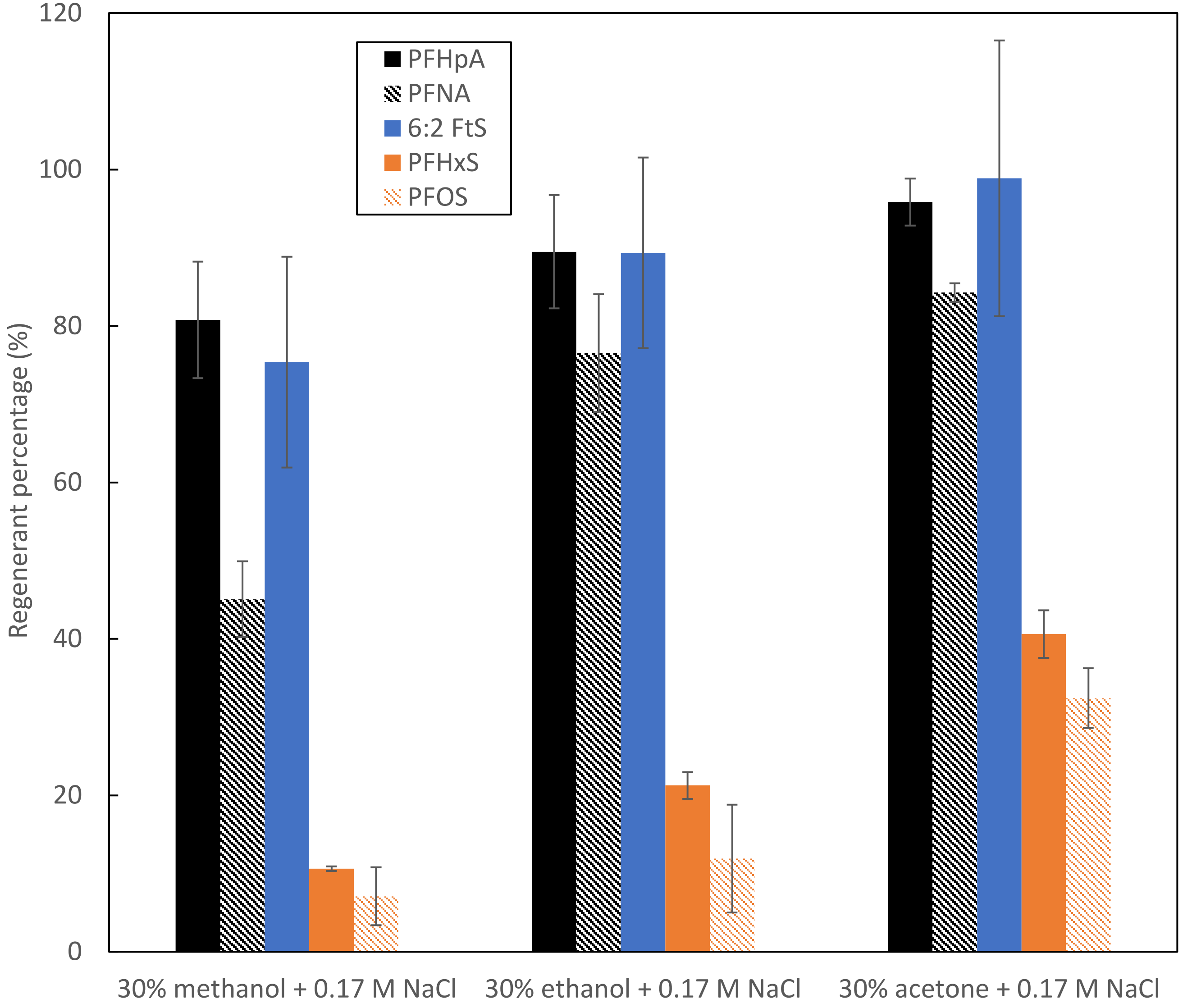
Batch regeneration cycles



- **No loss of regenerability after repeated cycles**

Solvent strength

- Compare methanol, ethanol, and acetone
- Less polar solvents more effective regeneration
- More research needed to assess impact on resin performance



Column regenerability

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- Atypical approach
  - Load PFAS in a large batch (20 !)
  - Transfer resin into column – all resins in column has same PFAS concentration (not breakthrough smear)
  - Apply flow-through MeOH/NaCl regenerant and monitor effluent

Prepare artificial groundwater (AGW) with resins and 14-PFAS suite

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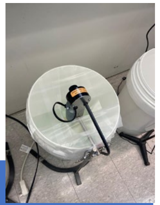


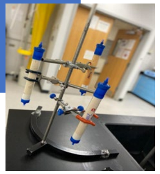
Equilibrate resins and PFAS with AGW for 7 days

↓

Separate resins than AGW.

→

Add saturated resin to column, and run the column



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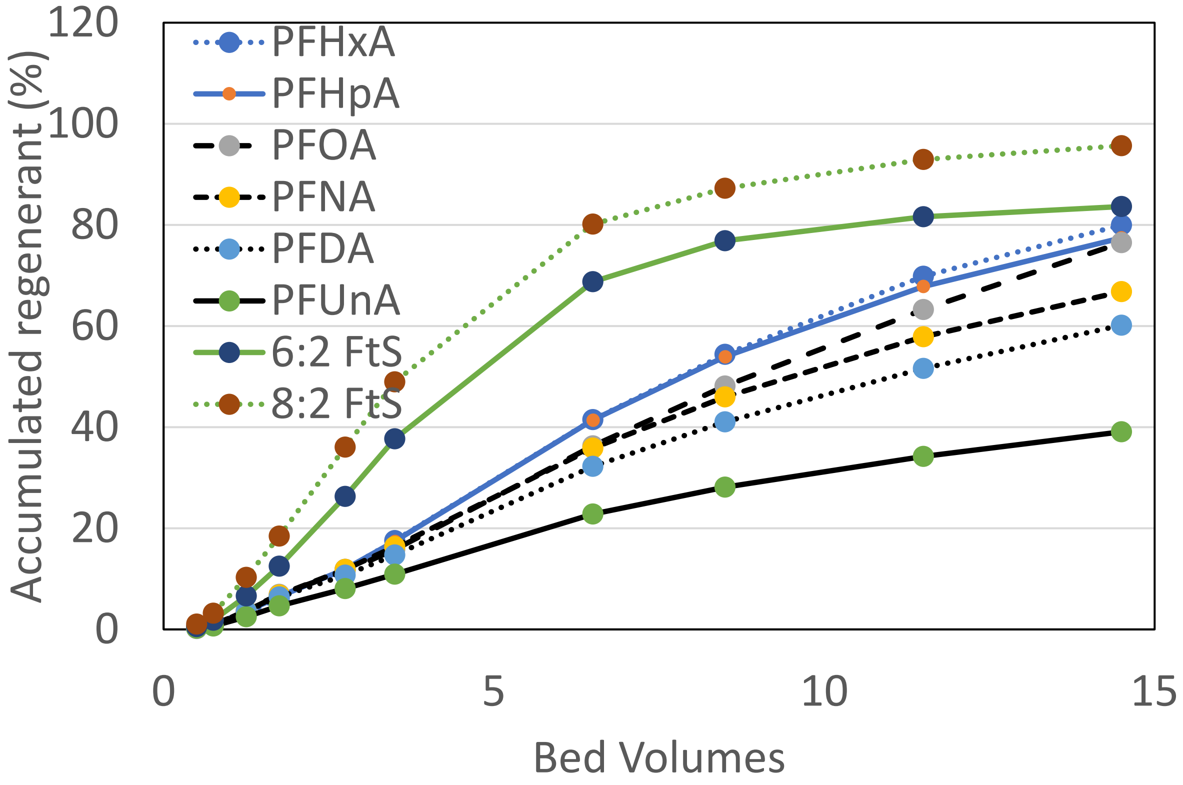
Do SPE extraction
- Regenerant solution

→

QTOF analysis
- Regenerant solution

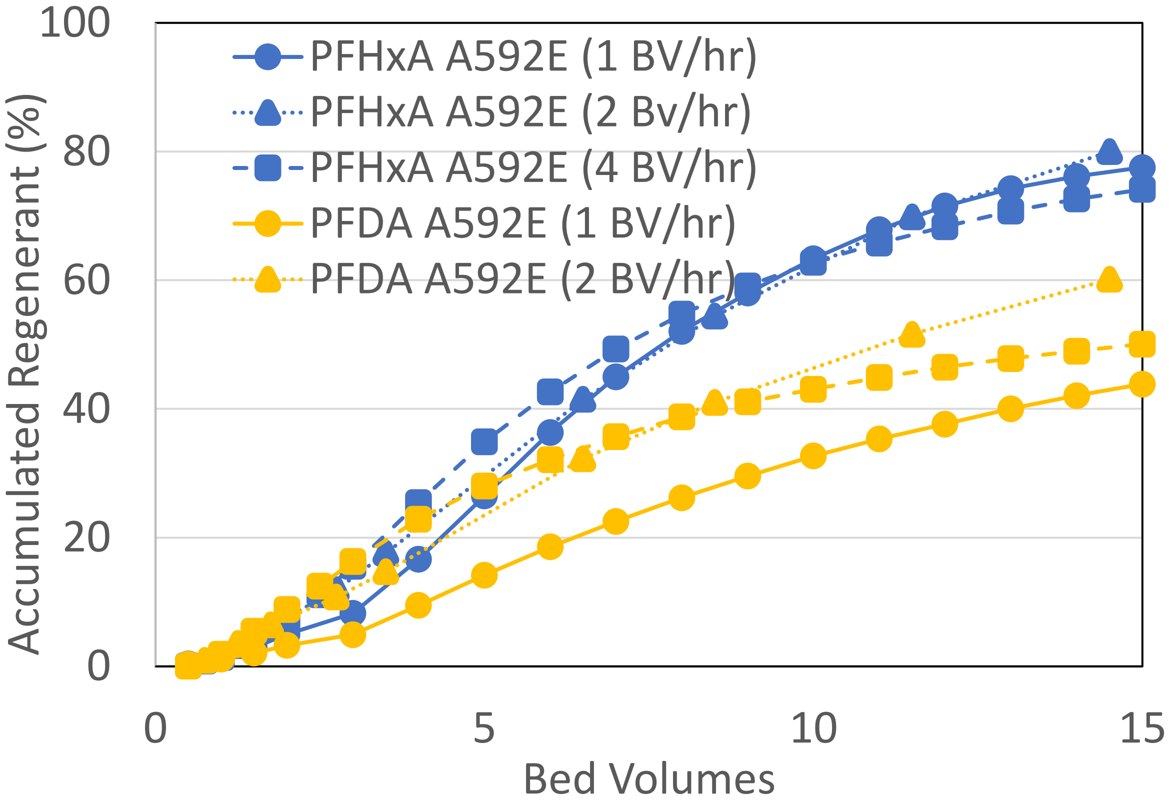
Process of the experiment design (column reactor)

Column regenerability



- FtS > PFCA >> PFSA
  - PFSA ineffective (<10%)
- Chain length elution effect

- Two cycle regeneration did not show a strong effect (not shown)
- Flow rate not have a strong effect



Reflections

- Resins – regenerable option?
  - Can outperform AC for shorter chain length
  - Regenerability – depends on resin, salt, and solvent
  - Considerations: effectiveness, cost, safety, others (?)
- The dual role of salt
  - Needed as an exchange ion
  - Changes solution interactions
  - Currently looking at the solution side and effects on solubility
- Organic solvents likely needed
  - Only short-chain PFCAs regenerated with brines
- Column regeneration testing results – some unexpected findings

Thank you for your time

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Resins

	PFA694E *	A592E	USA21107	USA28707	USA291597EPF	USA21217
Type	-	Marcroporous	Macroporous	Macroporous	Gel	Macroporous
Polymer	PS [a]	PS [a]	PS [a]	Pa [b]	PS [a]	PS [a]
Crosslinker	DVB [c]	DVB [c]	DVB [c]	DVB [c]	DVB [c]	DVB [c]
Appearance	Beads	Beads	Beads	Beads	Beads	Beads
Base Strength	Strong	Strong	Weak **	Strong	Strong	Weak **
Base Type	Amine	Amine	Amine	Amine	Amine	Amine
Ionic Form	-	Cl^- [d]	Fb[e]	Cl^- [d]	Cl^- [d]	Fb[e]
Total Capacity (Cl- form), eq/L	-	0.9	1.3 **	0.8	1.6	1.7 **
Moisture Retention (Cl- form), %	-	50-56	54-62	66-72	42-45	56-62
Single-use or regenerarable	Single use	Regenerable	Regenerable	Regenerable	Regenerable	Regenerable
Matrix pH impact on PFAS removal	No	No	Yes	No	No	Yes
Expected PFAS removal	Very High***	High	Low to Medium at Slightly Acidic pH	Low	Medium	Low to Medium at Slightly Acidic pH
Ease of regeneration with						
Salt-based solution	N/A ****	N/A	Medium	Medium	N/A	Medium
Solvent-based solution	Hard	Medium	Medium	Easy	Medium	Medium

* Proprietary structure; some resin properties not provided; [a] Polystyene; [b] Polyacrylic; [c] Divinylbenzene; [d] Chloride form; [e] Free base form

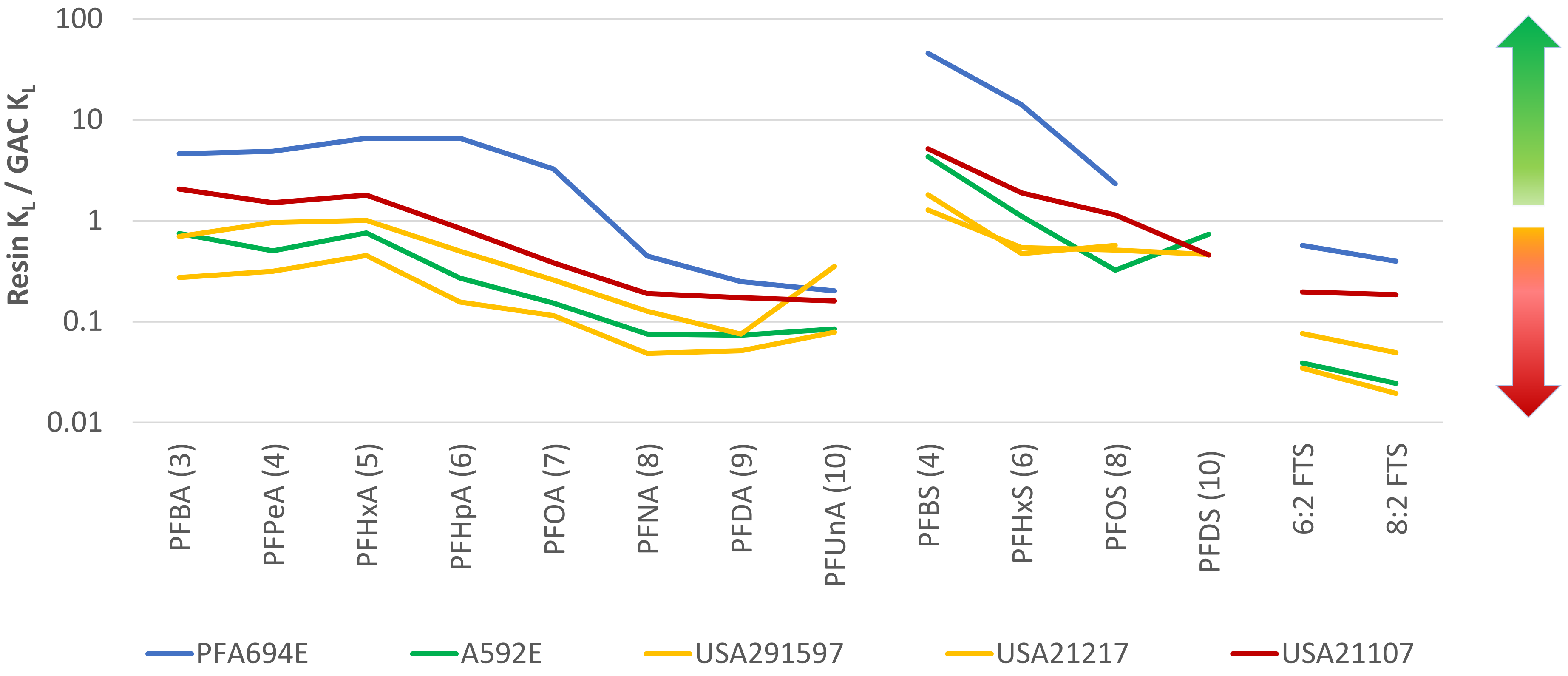
** Weak Base Resins should be partially protonated to work.

*** Assumed longer contact times.

**** Not applicable; not considered efficient.

Comparison to AC

- Comparison of linear isotherm K_L values – Resins vs. GAC



- ✓ **IX generally better removal for shorter chain length PFAS than GAC.**
- ✓ **Generally, resin performance:**

PFA694E > USA21107 > USA 21217 > A592E > USA 291597