Improving Activated Carbon Performance for In-Situ Sequestration of Per- and Polyfluoroalkyl Substances

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2023 Bioremediation Symposium

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Overview

- Permeable Adsorptive Barrier (PAB)
- Key Properties of Activated Carbons
- Stabilized-Powdered Activated Carbon (S-PAC)
- Carbon Properties: Pore Size and Distribution and Surface Properties
- PFAS Batch Adsorption Experiments
- PFAS Adsorption Results
- Push-pull Aquifer Cell Results

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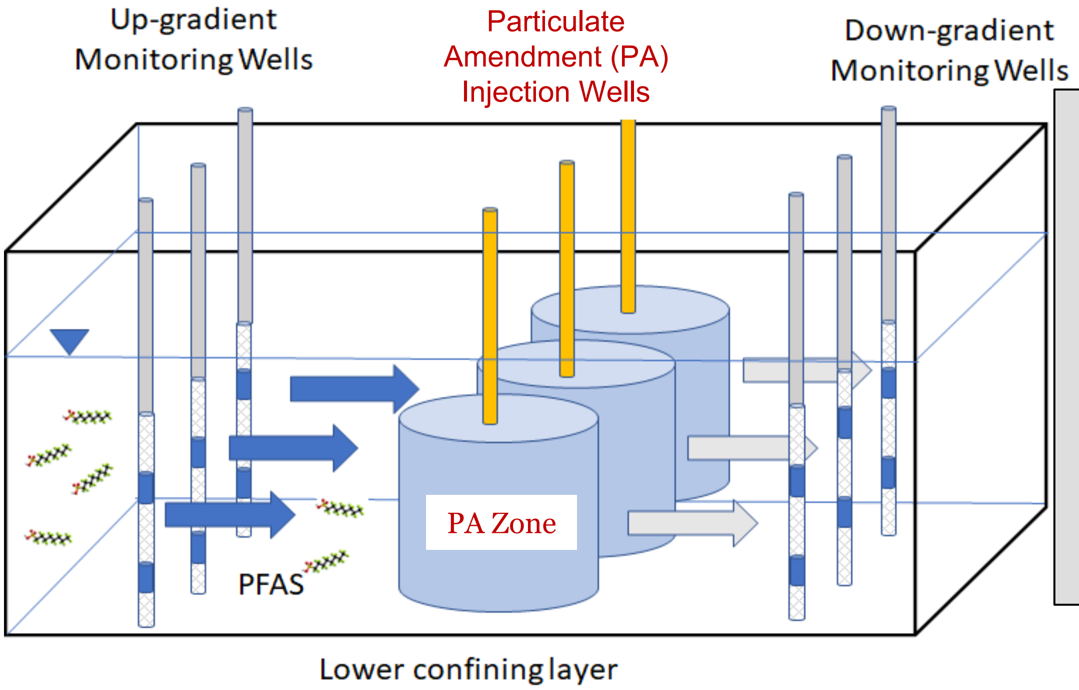
Permeable Adsorptive Barrier (PAB)



PA Delivery/Retention Goals

- "Intermediate" particle transport (1-3 m)
- High surface coverage/attachment
- Minimal permeability reductions
- No pore clogging/face-caking
- No particle detachment
- Possibility of in-situ regeneration
- Funnel and gate could be applied in shallow systems, allowing for amendment exchange/replacement

Key Properties for Maximizing Contaminant Retention by Activated Carbons

Surfaces

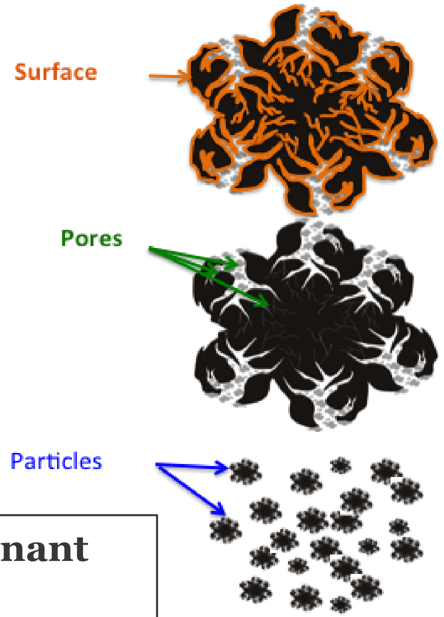
- Host for chemical reactants, catalysts, and chemical functionalities

Pores

- “Holes” of varying sizes to “transport” and “capture” target molecules to be removed

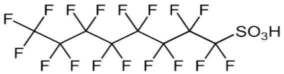
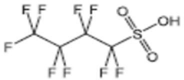
Particles

- Transportation medium to deliver desired properties to the right location at the right time



Tune carbon surfaces, pores, and particles to maximize contaminant adsorption

Matching PFAS Properties to Activated Carbon Features

	Molecular Size	Sequestration Pore Width (1-2x molecular diameter)	Transport Pore Width (up to 10x molecular diameter)	Charge	Hydrophobicity (log K_{ow})
PFOS  Perfluorooctane sulfonic acid	8 x 13 Å	8 - 26 Å	26 – 130 Å	Negative under most pH conditions	Very hydrophobic (5.6)
PFOA  Perfluorooctanoic acid	8 x 13 Å	8 - 26 Å	26 – 130 Å	Negative under most pH conditions	Hydrophobic (3.1)
PFBS  Perfluorobutane sulfonic acid	7 x 10 Å	7 - 20 Å	20 – 100 Å	Negative under most pH conditions	Marginally hydrophobic (2.6)

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Molecular diameters of targeted compounds give a first indication of the necessary carbon pore sizes for transport and sequestration while hydrophobicity and charge impact receptivity to capture

Research Objectives

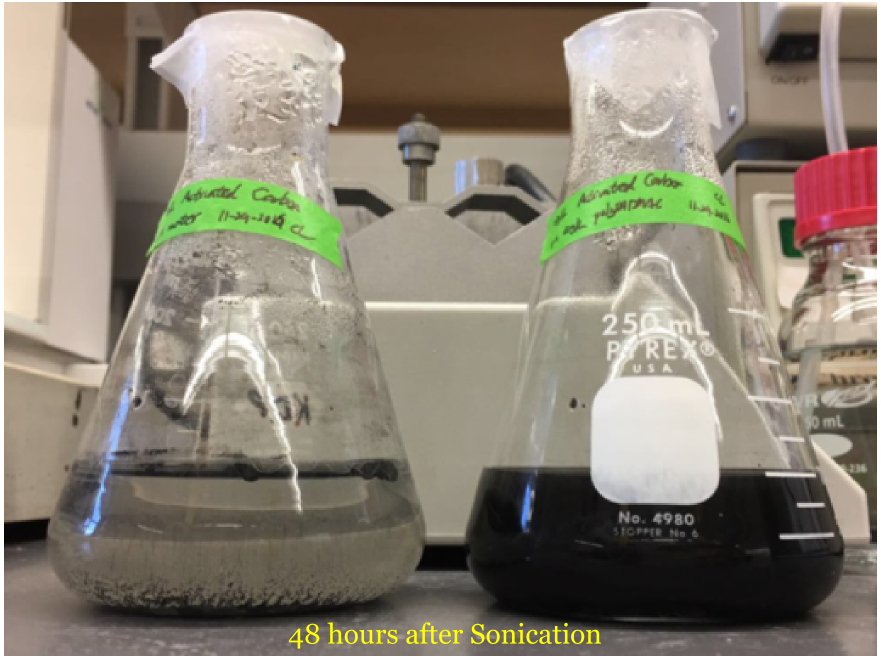
- Develop a fundamental understanding of the driving mechanisms and associated activated carbon (AC) features that govern adsorption of both long and short-chain PFAS
- Evaluate the effects of AC properties on PFAS (individual and mixtures) adsorption capacity
- Evaluate the effects of natural organic matter (NOM) on PFAS adsorption by AC
- Optimize AC for in-situ treatment of PFAS-impacted groundwater

Stabilized Powdered Activated Carbon (S-PAC)

1 g/L PAC   1 g/L PAC + 5 g/L PDM

Immediately after Sonication

1 g/L PAC   1 g/L PAC + 5 g/L PDM



48 hours after Sonication

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PolyDADMAC (PDM) polymer stabilizes PAC in suspension, facilitates delivery and retention
Both PDM and PAC can serve as sorbents (wider range of effectiveness)

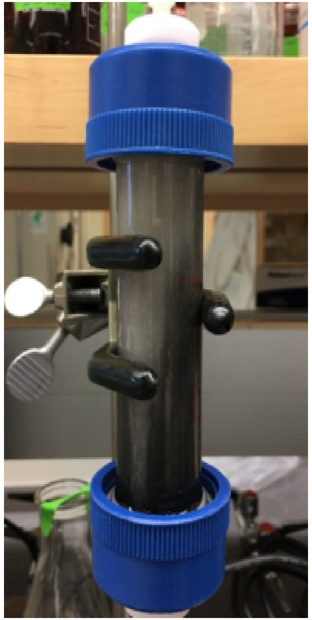
S-PAC Injection in 40-50 mesh Ottawa Sand

SERDP Project ER-2714

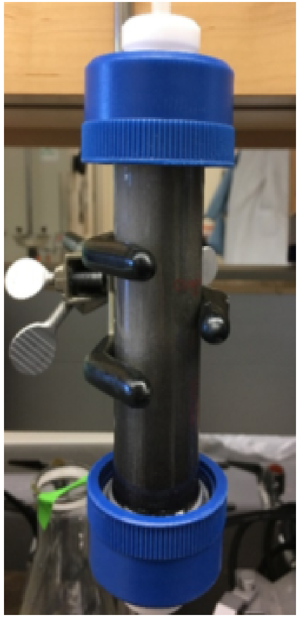
Flow Direction

t = 0 PV

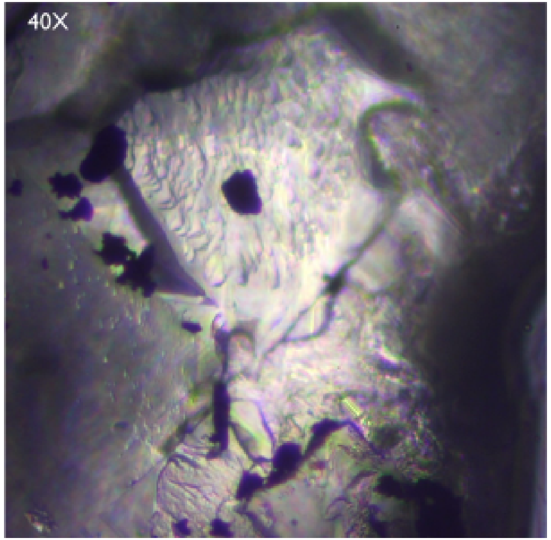
after 3.5 PV
PAC+PDM



after 3.5 PV
background



Leica DM IL LED



- 40-50 mesh Ottawa Sand (d_{50} = 358 um), $k_i = 7.37 \times 10^{-11}$ m², n = 0.37, SSA = 0.0125 m²/g
- PDM+PAC Suspension: 1,000 mg/L PAC + 5,000 mg/L PDM, viscosity = 1.18 cP
- Injection flow rate = 0.12 mL/min, pore-water velocity = 1.0 m/day

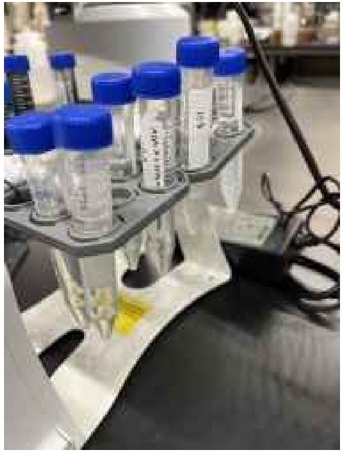
Carbon Properties

#	Description	Iodine number (mg/g)	Total Pore Volume <500Å cc/g	Micro Pore Volume <20Å cc/g	Small Meso Pore Volume <20-150Å cc/g	pH Point of Zero Charge	Hydrophilic Surface Functionality (Micro TGA wt% loss)	Ash (dry wt%)
A	Lignite-based mesoporous carbon	573	0.66	0.21	0.20	11.9	0.90	27.5
C	Bituminous-based micro and mesoporous carbon	980	0.57	0.33	0.17	9.8	0.38	8.4
G	Developmental Bituminous-based micro and mesoporous carbon	1009	0.69	0.39	0.17	TBD	0.19	5.0

Seven carbons were evaluated (A-H), and based on PFOA adsorption capacity, Carbons A, C, and G were selected for additional testing.

PFAS Batch Adsorption Experiments

- Dilute 2 mL of the original carbon slurry to 50 mL to achieve AC conc. of 2,000 mg/L
- Prepare solutions of PFOA/PFBS/PFOS individually or as a mixture at concentrations of 10 ug/L to 10,000 ug/L
- Mix 1 mL diluted AC with 9 mL of PFAS solution in triplicate and vortex
- Mix on rotary shaker for 7 days
- Centrifuge at 3,000 rpm for 30 mins
- Filter supernatant
- Analyze for PFAS using Waters LC-MS/MS



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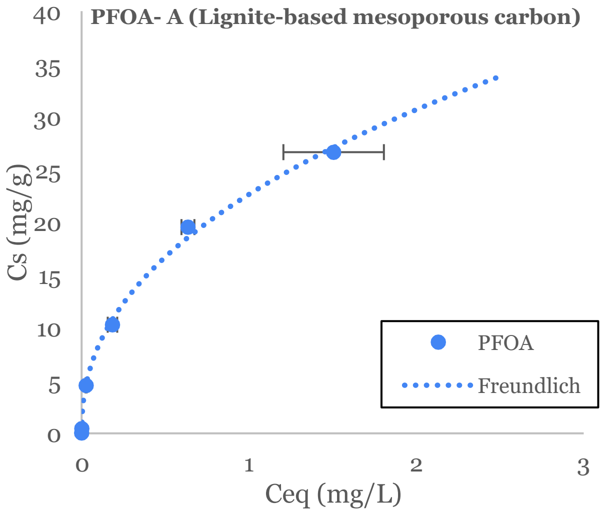
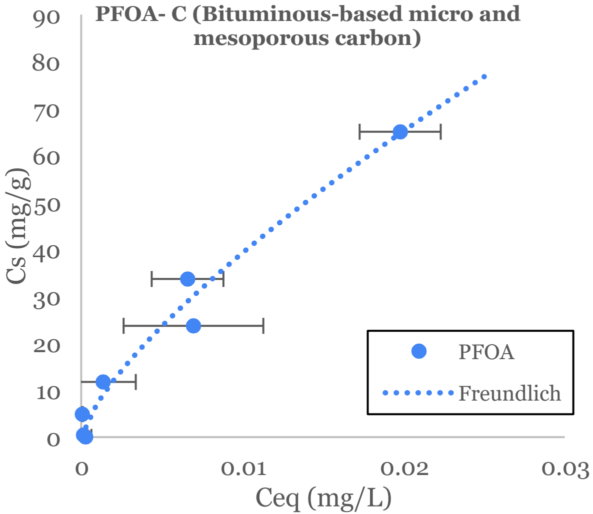
Single Solute PFOA Adsorption



$K_f = 22.64 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.44

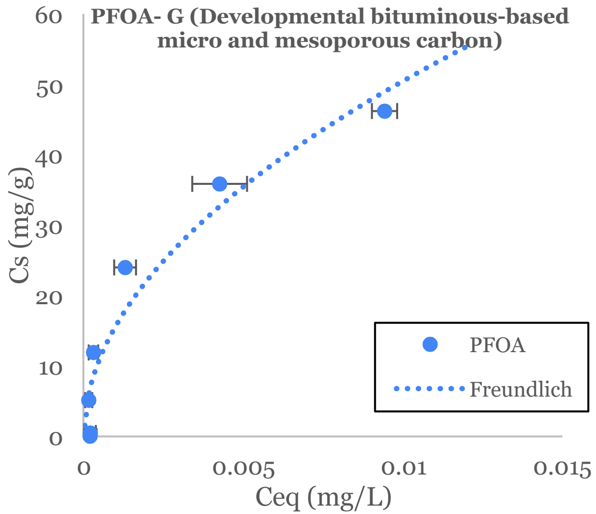
$r^2 = 0.997$



$K_f = 1147.03 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.73

$r^2 = 0.971$



$K_f = 528.13 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.51

$r^2 = 0.919$

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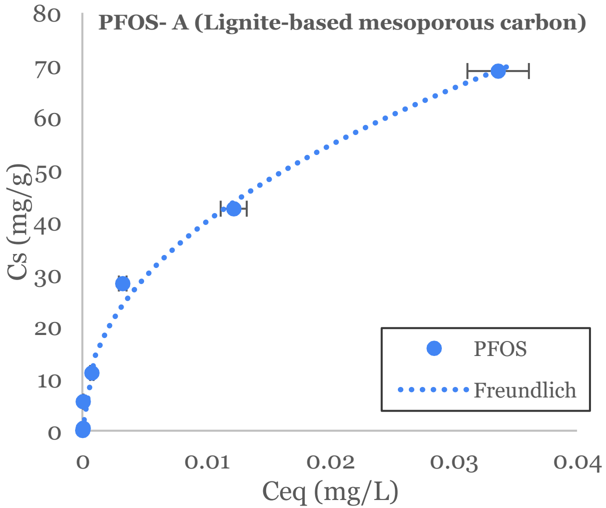
Carbon C exhibited highest adsorption capacity of PFOA alone.
For example, at Ceq = 100 ug/L; A = 8.26 mg/g; C = 202.86 mg/g; G = 163.21 mg/g

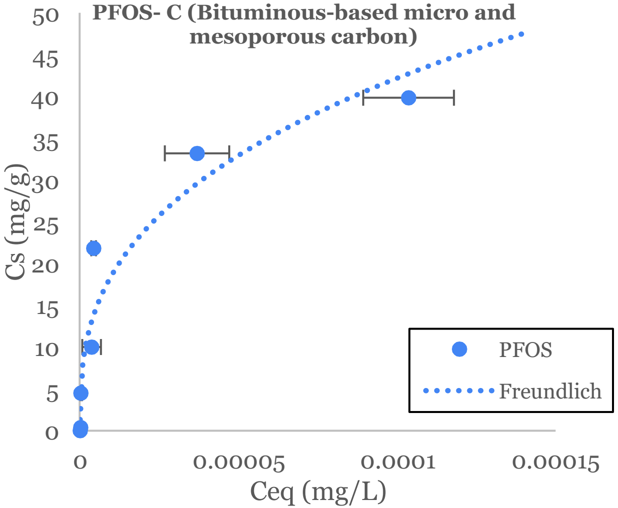
Single Solute PFOS Adsorption



$K_f = 318.73 \frac{mg}{g}\frac{L}{mg}^{n}$

$n = 0.45$

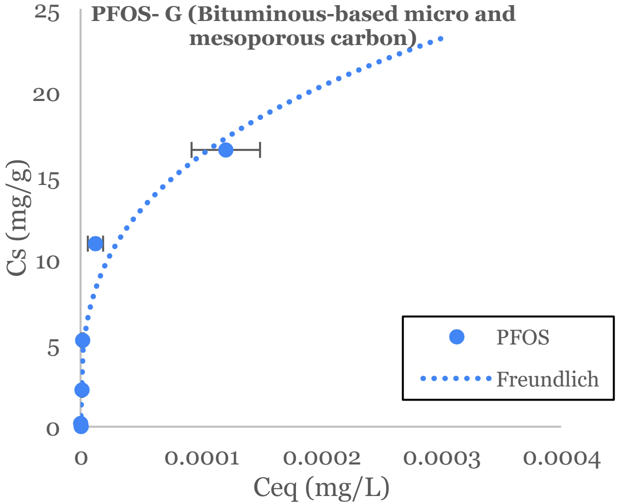
$r^2 = 0.989$



$K_f = 1129.62 \frac{mg}{g}\frac{L}{mg}^{n}$

$n = 0.36$

$r^2 = 0.909$



$K_f = 326.81 \frac{mg}{g}\frac{L}{mg}^{n}$

$n = 0.33$

$r^2 = 0.919$

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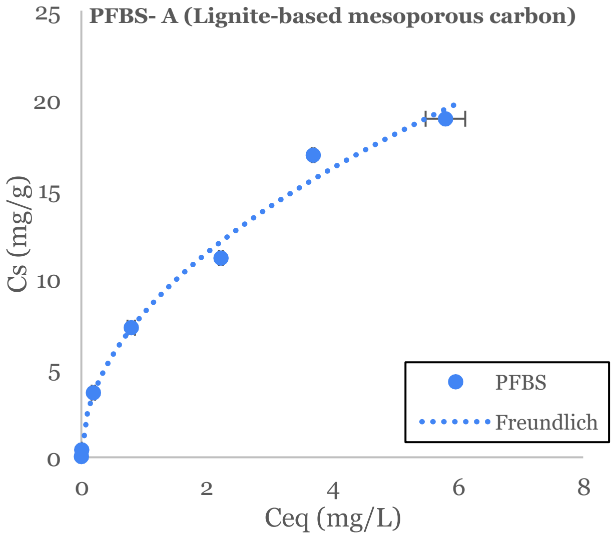
Carbon C exhibited highest adsorption capacity of PFOS alone.
For example, at Ceq = 100 ug/L; A = 112.83 mg/g; C = 496.51 mg/g; G = 154.27 mg/g

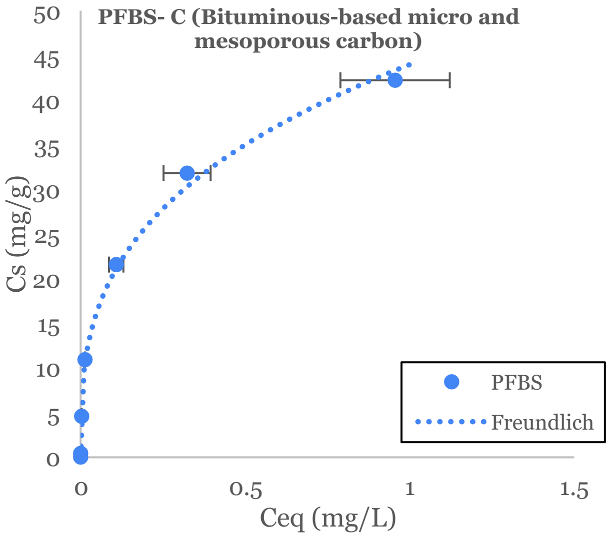
Single Solute PFBS Adsorption



$K_f = 8.09 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.50

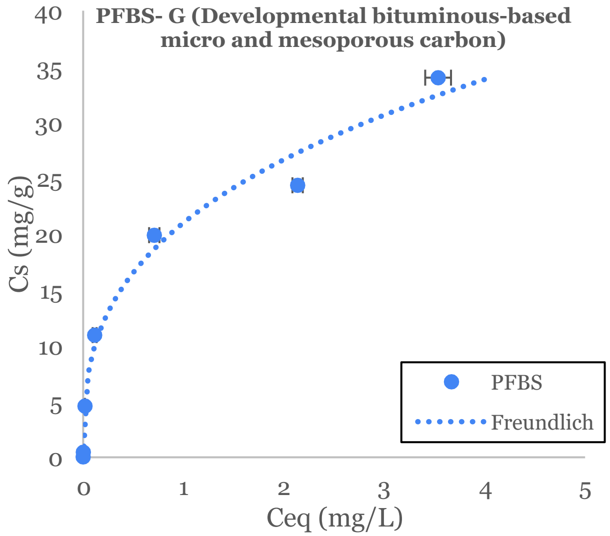
r^2= 0.991



$K_f = 43.96 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.33

r^2= 0.994



$K_f = 21.01 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.34

r^2= 0.985

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Carbon C exhibited highest adsorption capacity of PFBS alone.
For example, at Ceq = 100 ug/L; A = 2.56 mg/g; C = 20.56 mg/g; G = 9.51 mg/g

PFOA/PFOS/PFBS Mixture Adsorption (Carbon A)

PFOS:

$K_f = 83.63 \frac{mg}{g}\frac{L}{mg}^{n}$

n= 0.43

$r^2 = 0.948$

PFOA:

$K_f = 30.50 \frac{mg}{g}\frac{L}{mg}^{n}$

n= 0.37

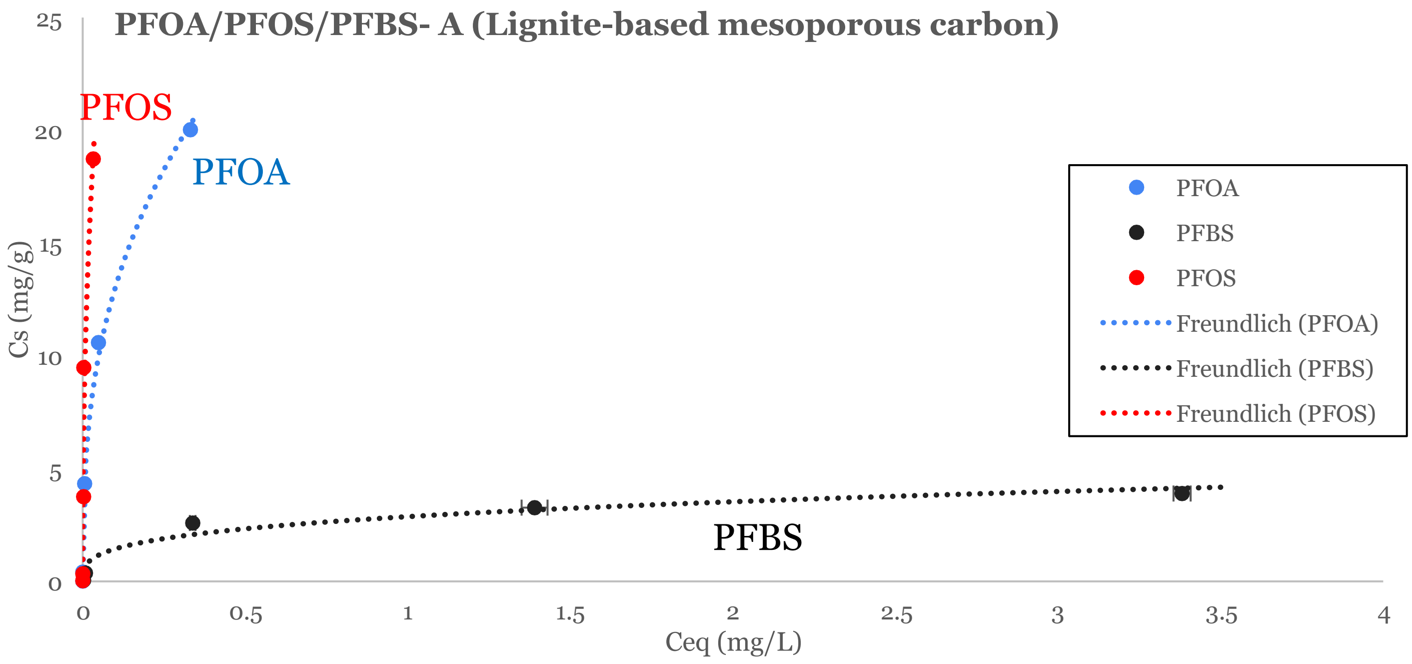
$r^2 = 0.995$

PFBS:

$K_f = 2.87 \frac{mg}{g}\frac{L}{mg}^{n}$

n= 0.30

$r^2 = 0.949$



Carbon A had greatest adsorption of PFOS in PFAS mixture

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PFOA/PFOS/PFBS Mixture Adsorption (Carbon C)

PFOS:

$K_f = 736.26 \frac{mg}{g} \frac{L}{mg}^n$

n= 0.33

$r^2 =$ 0.939

PFOA:

$K_f = 70.65 \frac{mg}{g} \frac{L}{mg}^n$

n= 0.33

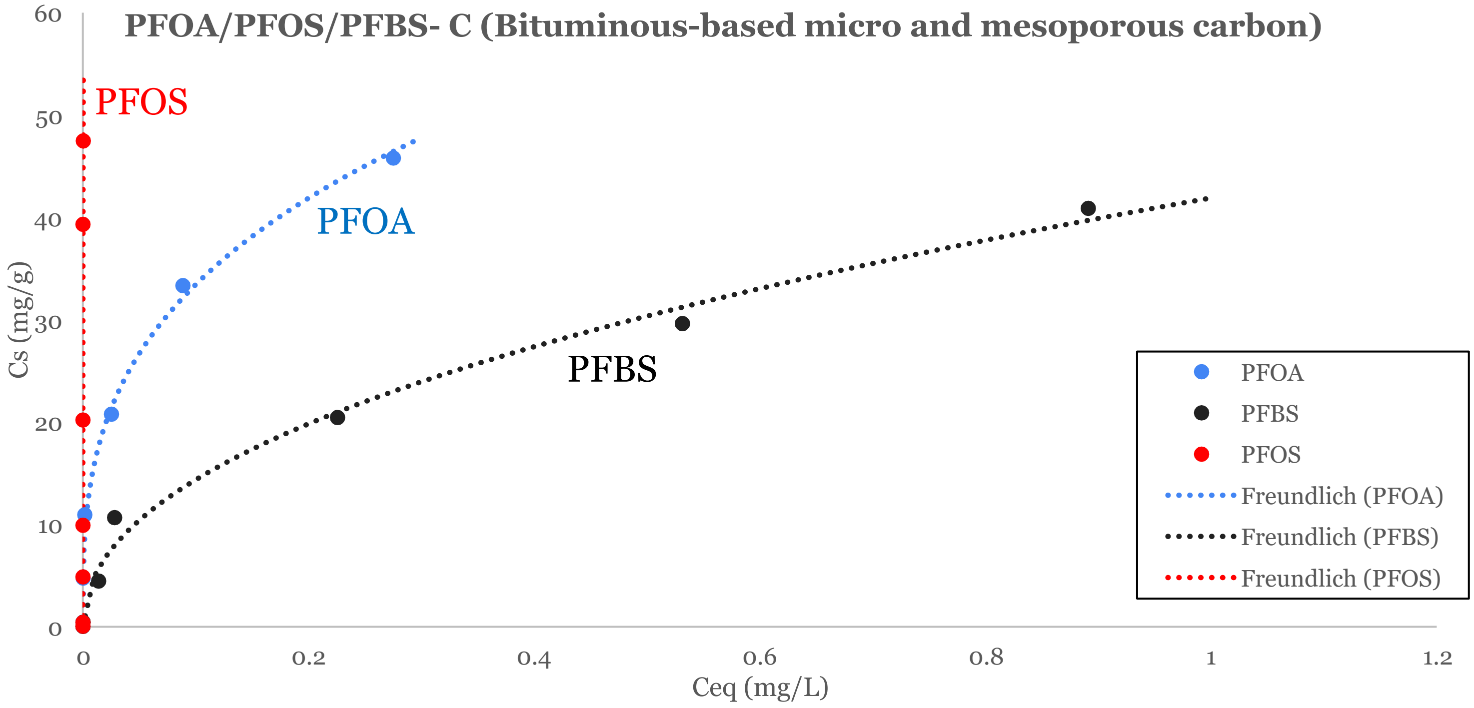
$r^2 =$ 0.991

PFBS:

$K_f = 41.90 \frac{mg}{g} \frac{L}{mg}^n$

n= 0.47

$r^2 =$ 0.991



Carbon C had greatest adsorption of PFOS in PFAS mixture, and exhibited greater adsorption of each PFAS than Carbon A

PFOA/PFOS/PFBS Mixture Adsorption (Carbon G)

PFOS:

$K_f = 118.28 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.20

r^2= 0.983

PFOA:

$K_f = 82.64 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.33

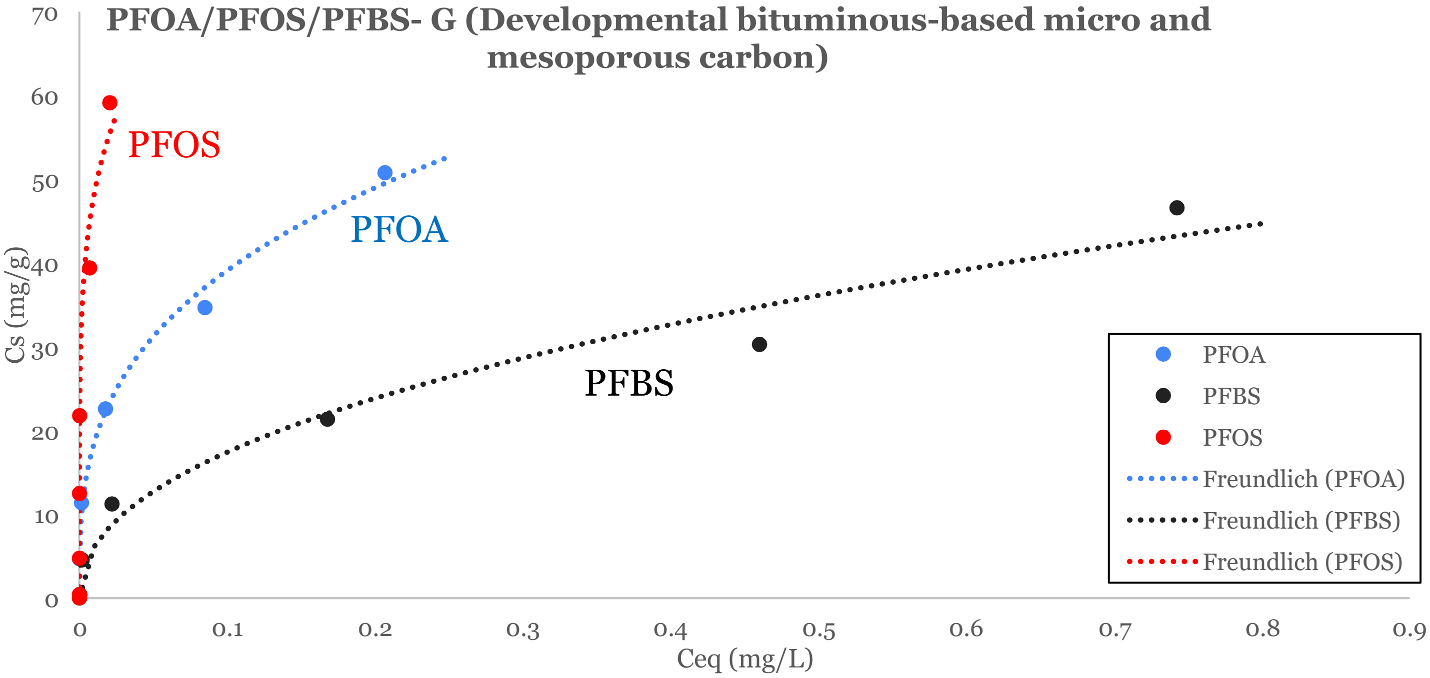
r^2= 0.993

PFBS:

$K_f = 49.45 \frac{mg}{g}\frac{L}{mg}^n$

n= 0.45

r^2= 0.977



Carbon G exhibited the greatest adsorption of PFOS in PFAS mixture, and exhibited greater adsorption of PFOA and PFBS than either Carbon A or Carbon C

Comparison of Single PFAS vs Mixture Adsorption Parameters

Carbon		Single solute PFAS adsorption			PFAS mixture adsorption		
		PFOA	PFOS	PFBS	PFOA	PFOS	PFBS
A (Lignite-based mesoporous carbon)	K_f	22.64	318.73	8.09	30.50	83.63	2.87
	n	0.44	0.45	0.50	0.37	0.43	0.30
	r^2	0.997	0.989	0.991	0.995	0.948	0.949
C (Bituminous-based micro and mesoporous carbon)	K_f	1147.03	1129.62	43.96	70.65	735.26	41.90
	n	0.73	0.36	0.33	0.33	0.33	0.47
	r^2	0.971	0.909	0.994	0.991	0.939	0.991
G (Developmental bituminous-based micro and mesoporous carbon)	K_f	528.13	326.81	21.01	82.64	118.28	49.45
	n	0.51	0.33	0.34	0.33	0.20	0.45
	r^2	0.919	0.919	0.985	0.993	0.983	0.977

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Carbon C and Carbon G have similar performances in PFAS mixtures and both perform better than Carbon A; Adsorption capacity in mixtures is generally lower than for single solutes; Presence of competing compounds has a higher impact on adsorption capacity at higher concentrations than lower concentrations

PFOA/PFOS/PFBS/NOM Mixture Adsorption (Carbon A)

PFOS:

$K_f = 126.80 \frac{mg}{g} \frac{L}{mg}^{n}$

n= 0.18

$r^2 =$ 0.767

PFOA:

$K_f = 18.70 \frac{mg}{g} \frac{L}{mg}^{n}$

n= 0.19

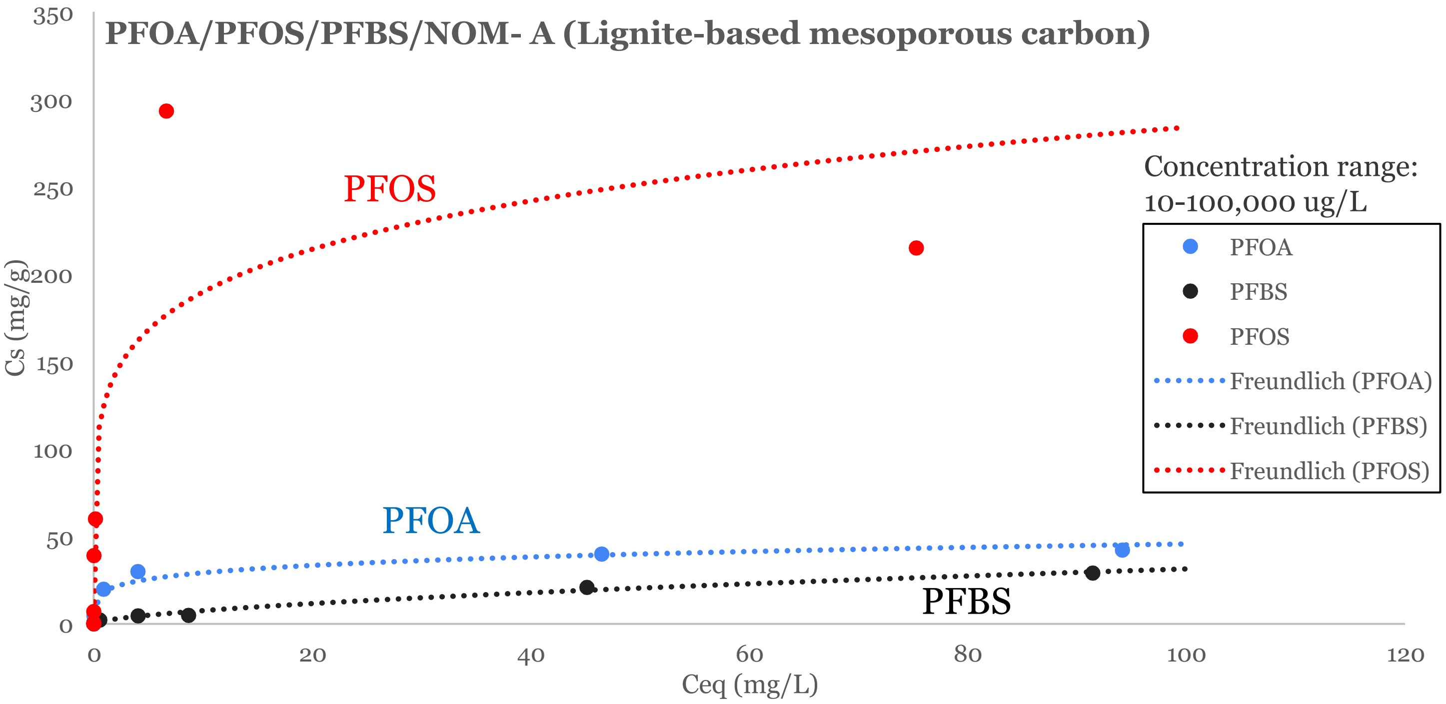
$r^2 =$ 0.963

PFBS:

$K_f = 1.83 \frac{mg}{g} \frac{L}{mg}^{n}$

n= 0.62

$r^2 =$ 0.989



In the presence of 12 mg/L NOM, Carbon A still exhibited greater adsorption of PFOS from the PFAS mixture, but was reduced

Comparison of PFAS Mixture Adsorption Parameters with and without Natural Organic Matter

Carbon		With NOM			Without NOM		
		PFOA	PFOS	PFBS	PFOA	PFOS	PFBS
A (Lignite-based mesoporous carbon)	K_f	18.70	126.80	1.83	30.50	83.63	2.87
	n	0.19	0.18	0.62	0.37	0.43	0.30
	r^2	0.963	0.767	0.989	0.995	0.948	0.949

Comparison of Cs values at Ceq= 0.1 mg/L	With NOM			Without NOM		
	PFOA	PFOS	PFBS	PFOA	PFOS	PFBS
	11.96 mg/g	84.75 mg/g	0.44 mg/g	13.01 mg/g	30.78 mg/g	1.44 mg/g

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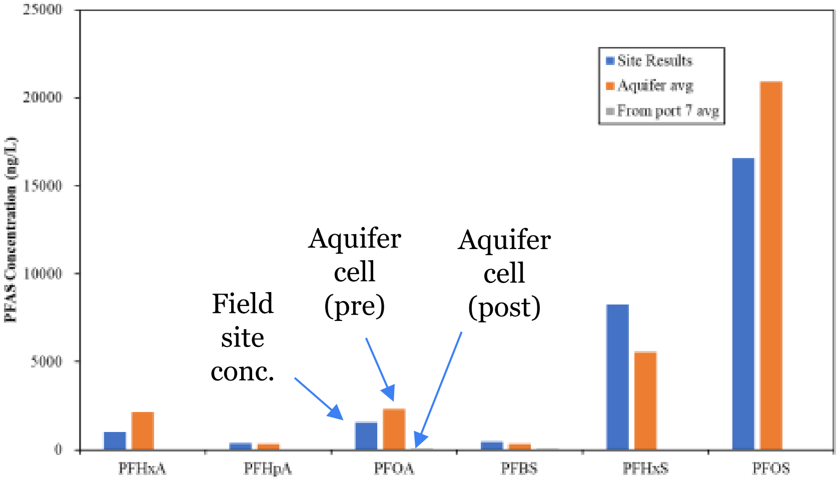
At 100 ug/L, NOM competed for adsorption sites, resulting in 70% decrease in PFBS adsorption

Push-Pull Aquifer Cell Test of FluxSorb IS (Carbon A)

Aquifer Cell Test (Push Phase)

Pre- and Extracted (Pull Phase) PFAS Concentrations



NESDI Project 5771

Advanced Emissions Solutions, Inc. Advancing Cleaner Energy

FluxSorb TECHNOLOGIES PART OF THE ADVANCED EMISSIONS SOLUTIONS, INC GROUP OF COMPANIES

90-99.9% PFAS Removal

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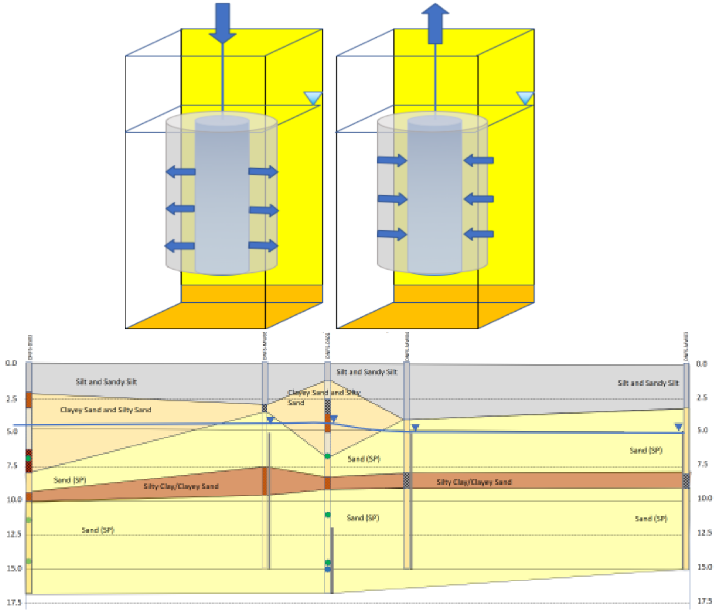
Partnered with ADES (Joe Wong and Micala Mitchek) to develop S-PAC at a commercially-available scale

FluxSorb IS Push-Pull Field Demonstration

- Drive push injection (DPT) of 500 gal (5 g/L PAC + 5 g/L PDM) in two 4-ft intervals (250 gal each)
- Sampled from adjacent extraction well after recovering 1200, 1350 gal, 1500 gal of water



Pre-treatment PFAS Concs. (ng/L)		Post-Treatment PFAS Concs. (ng/L) Volume Extracted					
Analyte	Ave.	742 gal	908 gal	1058 gal	1208 gal	1350 gal	1500 gal
PFPeA	120	2.88	<2.4	<2.4	<2.4	<2.4	<2.4
PFHxA	150	2.22	<1.2	<1.2	<1.2	<1.2	<1.2
PFHpA	240	1.27	<1.2	<1.2	<1.2	<1.2	<1.2
PFHpS	740	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
6:2 FTS	1,620	3.00	<4.5	<4.5	<4.5	<4.5	<4.5
PFBS	1,760	3.50	<1.1	<1.1	<1.1	<1.1	<1.1
PFPeS	1,820	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
PFOA	2,790	5.57	<1.2	<1.2	<1.2	<1.2	<1.2
FOSA	4,280	1.53	<1.2	<1.2	<1.2	<1.2	<1.2
PFHxS	10,100	6.85	<1.1	<1.1	<1.1	<1.1	<1.1
PFOS	28,280	15.51	<1.1	<1.1	<1.1	<1.1	<1.1

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Post-treatment PFAS concentrations were below detection limits after extracting approximately 900 gallons of groundwater, and remained below detection limits for duration of test

Key Findings

- Carbon C (bituminous-based micro and mesoporous carbon) exhibited the greatest adsorption of each single solute PFAS
- Carbon G (developmental bituminous-based micro and mesoporous carbon) exhibited the greatest adsorption of PFOA and PFBS in the PFAS mixture
- Carbon G and Carbon C perform similarly and both outperform Carbon A in PFAS mixture systems
- In PFAS mixture systems, the presence of competing compounds impacts the adsorption capacity at higher concentrations but has little to no impact at lower concentrations
- In PFAS mixtures with NOM, NOM competes for adsorption sites and lowers the adsorption capacity of PFOA and PFBS
- Successful removal of PFAS from groundwater using Carbon A applied in the field

Acknowledgements

- ADES: Dr. Joe Wong and Micala Mitchek
- Dr. Kurt Pennell
- Dr. Katherine Manz
- Chloe Gray
- Drs. James Hatton (Jacobs), Matt Simcik (UMinn) and Bill Arnold (UMinn)
- Drs. Jovan Popovic and Ben Rhiner (NESDI)

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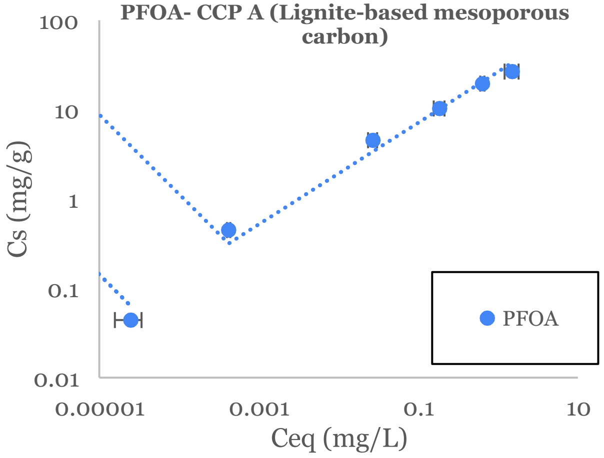
Questions

Backup Slides

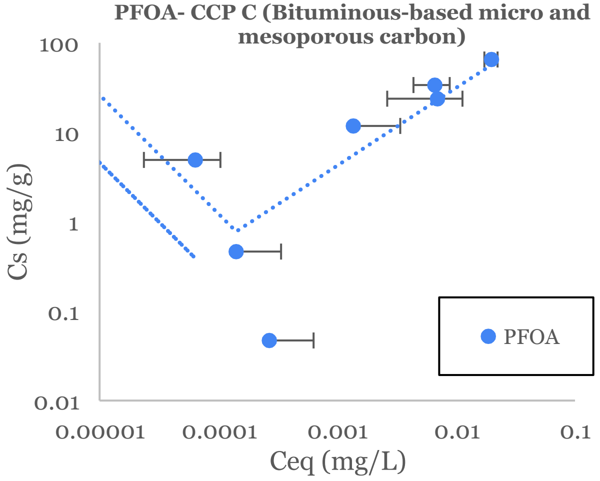
Single Solute PFOA Adsorption



$K_f = 22.637 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.438

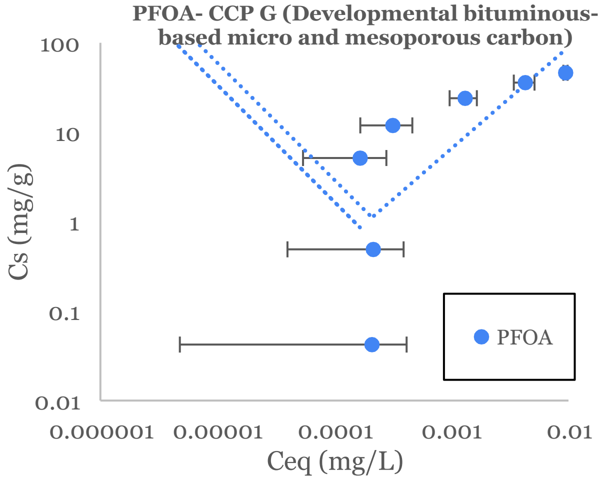
$r^2 = 0.997$



$K_f = 1147.03 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.733

$r^2 = 0.971$

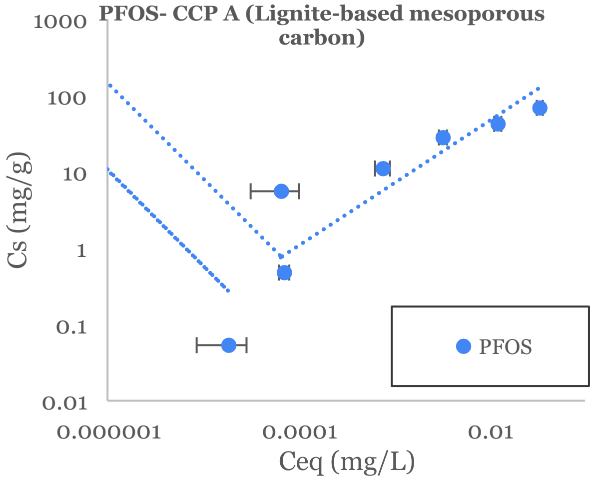


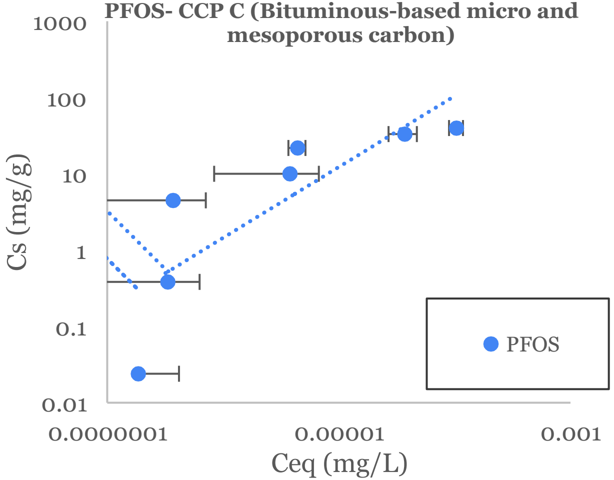
$K_f = 528.133 \frac{mg}{g}\frac{L}{mg}^{1/n}$

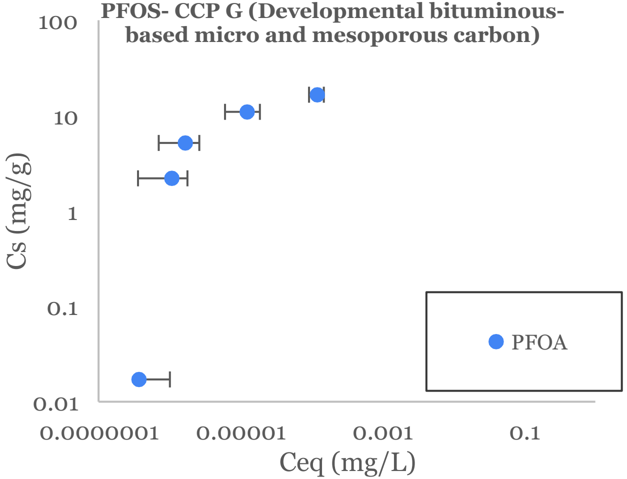
n= 0.510

$r^2 = 0.919$

Single Solute PFOS Adsorption





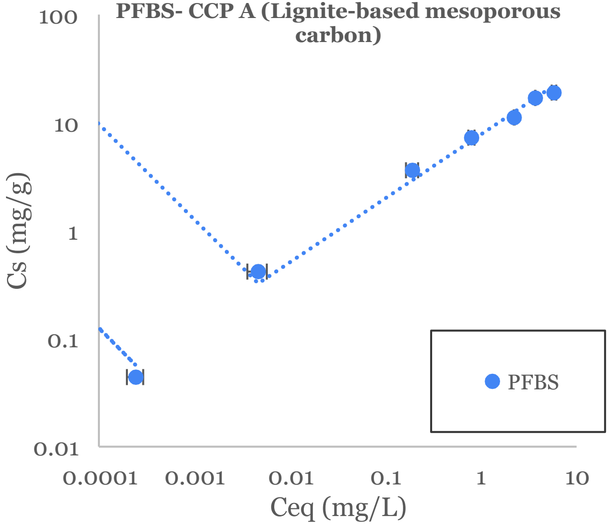


$K_f = 318.726 \frac{mg}{g} \frac{L}{mg}^{1/n}$
n= 0.451
r^2= 0.989

$K_f = 1129.619 \frac{mg}{g} \frac{L}{mg}^{1/n}$
n= 0.357
r^2= 0.909

$K_f = 326.806 \frac{mg}{g} \frac{L}{mg}^{1/n}$
n= 0.326
r^2= 0.919

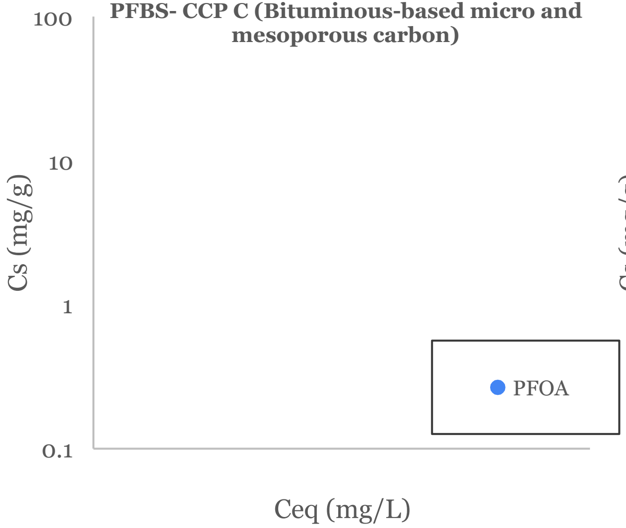
Single Solute PFBS Adsorption



$K_f = 8.090 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.5

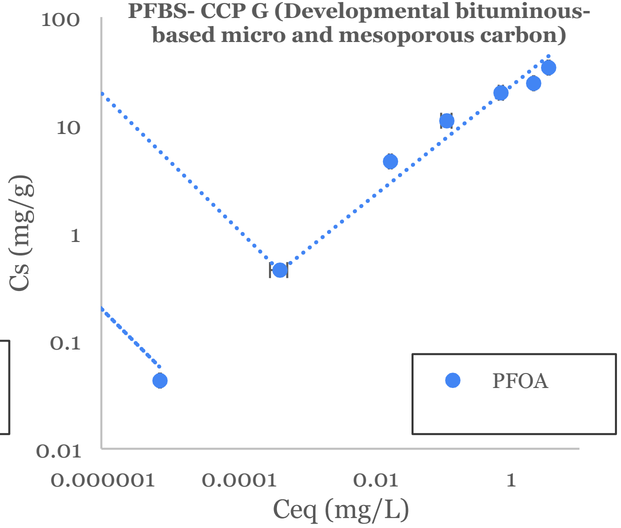
$r^2 =$ 0.991



$K_f = 43.963 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.33

$r^2 =$ 0.994



$K_f = 21.007 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.344

$r^2 =$ 0.985

PFOA/PFOS/PFBS Mixture Adsorption (CCP-A)

PFOA:

$K_f = 30.499 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.37

$r^2 = 0.995$

PFOS:

$K_f = 83.625 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.434

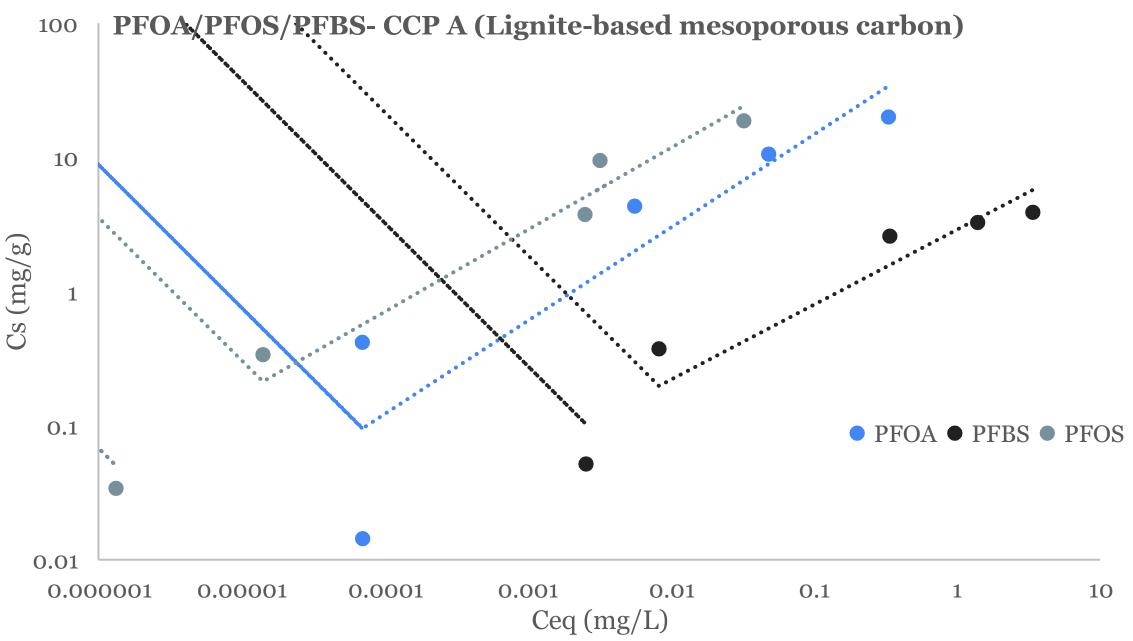
$r^2 = 0.948$

PFBS:

$K_f = 2.87 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.299

$r^2 = 0.949$



PFOA/PFOS/PFBS Mixture Adsorption (CCP-C)

PFOA:

$K_f = 70.648 \, \frac{mg}{g} \frac{L}{mg}^{1/n}$

n= 0.325

$r^2 = 0.991$

PFOS:

$K_f = 736.255 \, \frac{mg}{g} \frac{L}{mg}^{1/n}$

n= 0.334

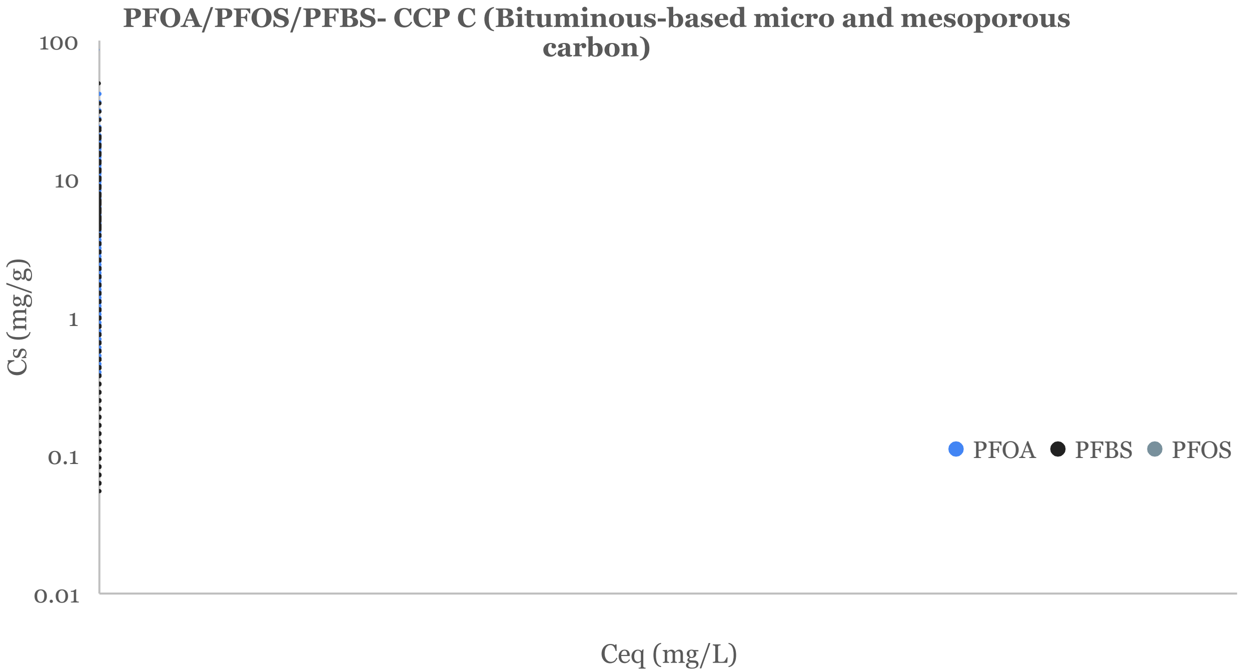
$r^2 = 0.939$

PFBS:

$K_f = 41.897 \, \frac{mg}{g} \frac{L}{mg}^{1/n}$

n= 0.465

$r^2 = 0.991$



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PFOA/PFOS/PFBS/NOM Mixture Adsorption (CCP-A)

PFOA:

$K_f = 18.694 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.194

r^2= 0.963

PFOS:

$K_f = 126.801 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.175

r^2= 0.767

PFBS:

$K_f = 1.825 \frac{mg}{g}\frac{L}{mg}^{1/n}$

n= 0.618

r^2= 0.989