Supplementary Information

Absorption of Short-Chain to Long-Chain Perfluoroalkyl Substances Using Swellable Organically Modified Silica

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Table S1: Optimized MS(QqQ) parameters

Compound	MRM Transition (*m*/*z*)		MS Voltages		Mobile Phase	
	precursor	product(s)	fragmentor	CE	A%	B%
PFBA	213	168.9	50	8	70	30
PFPeA	263	218.9	60	8	53	47
PFHpA	362.9	319	72	0	37	63
		169		12		
PFHxA	313	268.9	70	8	44	56
		119		18		
PFOA	413	369	69	4	30	70
		169		12		
		80		41		
PFNA	462.96	419	80	9	27	73
PFDA	513	469	69	8	23	77
		218.7	100	16		
		219	80	13		
PFHxS	398.9	99	90	75	36	64
		80		41		
PFBS	298.9	98.9	69	32	52	48
		79.9		44		
PFOS	498.9	99	100	50	27	73
		80				
PFOSA	497.9	77.9	69	40	21	79
		47.9	100	100		
PFOSaAm	599	SIM	135		23	77

Table S2: Gradient HPLC method for separation of PFAS mixtures

time (min)	Mobile Phase Composition (%)	
	5mM ammonium acetate in H_2O	5mM ammonium acetate in 95% MeOH%
0	70	30
3	70	30
5	40	60
21	20	80
23	0	100
25	0	100

Table S3. Limits of detection for direct injection analysis by LC-MS

Analyte	MRL (μg/L)	LOD (μg/L)	Precision at MRL
PFDA	0.65	0.35	<2%
PFNA	0.65	0.35	<2%
PFOA	1.25	0.35	<2%
PFHpA	1.25	0.35	<3%
PFHxA	3.5	0.65	<3%
PFPeA	3.5	0.65	<3%
PFBA	6.5	1.25	<3%
PFOS	0.65	0.35	<3%
PFHxS	1.15	0.35	<3%
PFBS	1.25	0.35	<2%
PFOSA	3.5	0.65	<3%
PFOSaAm	3.5	0.65	<3%

MRL: Minimum reporting limit.
LOD: Limit of detection.

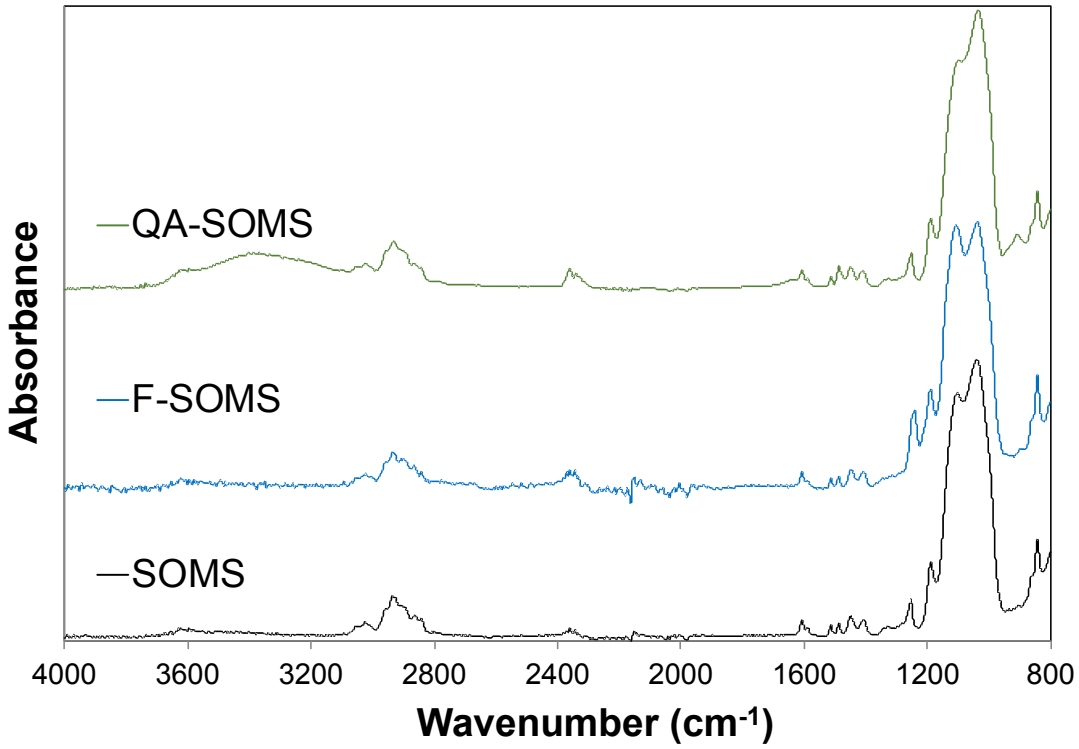

Figure S1: FT-IR spectra of SOMS adsorbents.

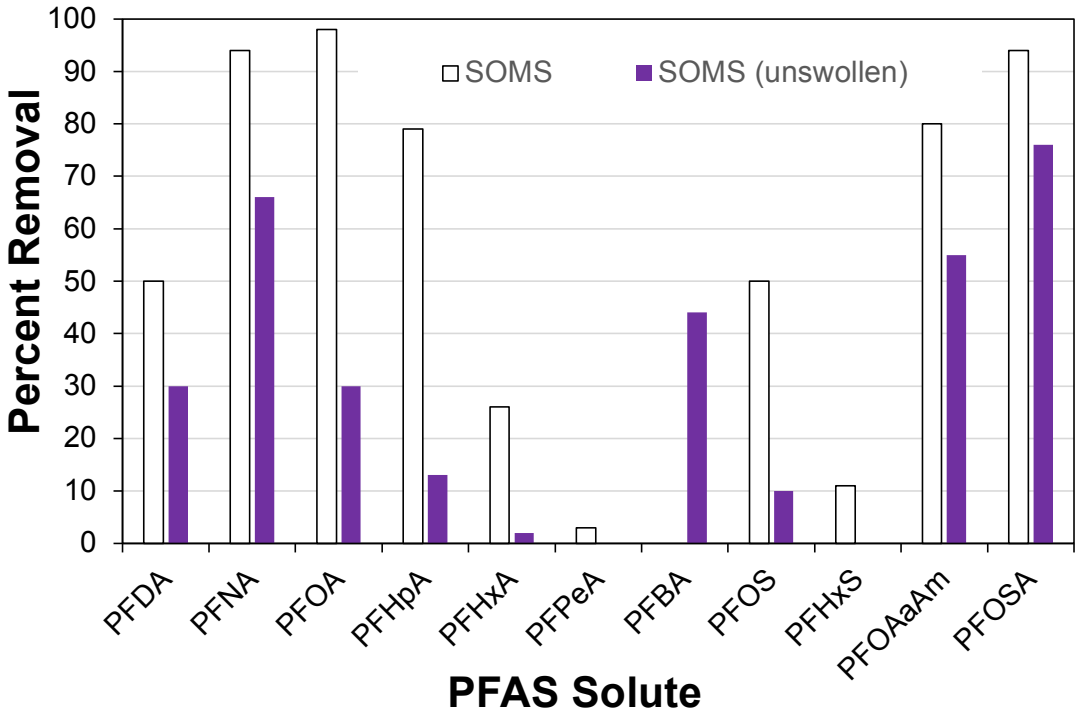

Figure S2: Percent removal of PFAS substance as a function of SOMS swollen state. PFBA is strongly removed by non-swollen SOMS. Swollen SOMS show no adsorption for PFBA.

Table S4. Second order rate constants for PFAS adsorption and the associated error.

	k_2 (g adsorbent/mgPFAS•hr)									
	ionic strength = 0 mM					ionic strength = 50 mM				
PFAS	**SOMS**	**F-SOMS**	**QA-SOMS**	**poly-SOMS**	**GAC**	**SOMS**	**F-SOMS**	**QA-SOMS**	**poly-SOMS**	**GAC**
PFDA	5.6±3.1	1.9±0.4	0.7±0.2	1.1±0.2	0.8±0.2	>20	19.0±1.2	5.3±0.2	1.2±0.3	1.4±0.5
PFNA	1.0±0.3	0.7±0.3	4.9±0.7	1.2±0.6	0.9±0.2	8.2±1.7	4.0±0.9	10.5±6.1	1.4±0.3	1.4±0.4
PFOA	10.4±3.8	6.9±1.8	2.5±1.0	1.1±0.3	1.6±0.7	6.5±1.8	>20	1.9±0.6	0.6±0.1	0.7±0.3
PFHpA	6.3±0.8	3.2±0.5	0.4±0.1	1.0±0.2	0.2±0.1	3.2±0.8	8.8±2.6	2.4±0.3	0.7±0.1	0.4±0.2
PFHxA	1.7±0.4	2.4±0.5	0.3±0.2	0.7±0.1	1.0±0.5	3.1±2.3	3.6±1.8	2.1±0.7	0.2±0.2	0.4±0.3
PFPeA	5.0±3.8	*no ads*	1.1±0.5	0.9±0.1	0.4±0.1	>20	*no ads*	0.8±0.1	1.3±0.2	0.6±0.2
PFBA	*no ads*	*no ads*	1.0±0.5	1.0±0.1	0.7±0.1	*no ads*	*no ads*	0.7±0.3	2.2±0.2	0.8±0.3
PFOS	7.8±6.5	5.9±0.6	>20	1.9±0.1	0.2±0.1	14±0.8	26.3±3.5	20	3.1±0.7	22±7.6
PFHxS	4.0±2.2	2.4±0.7	>20	0.7±0.1	0.1±0.01	>20	8.7±1.0	16±3	0.9±0.3	10±0.1
PFBS	11±30	*no ads*	*n/m*	0.1±0.1	0.1±0.04	>20	*no ads*	*n/m*	0.7±0.2	0.6±0.2
PFOSA	5.2±1.3	2.6±1.3	>20	5.6±1.8	0.6±0.3	3.9±1.3	6.3±2.6	20	2.3±0.4	0.4±0.2
PFOSaAm	1.9±1.0	0.2±0.3	>20	1.1±0.6	0.3±0.06	20±0.3	0.3±0.1	12±3	1.6±0.2	1.4±0.4

Table S5. Equilibrium adsorption capacities (q_e) calculated from second order kinetics and the associated error.

PFAS	q_e (mg/g)									
	ionic strength = 0 mM					ionic strength = 50 mM				
	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC
PFDA	5.0±0.4	5.8±0.1	6.0±0.4	10.0±0.3	7.5±0.3	9.9±0.1	10.0±0.1	6.2±0.1	9.9±0.3	9.9±0.4
PFNA	9.2±0.5	8.9±1.0	8.3±0.1	9.1±0.7	6.5±0.3	9.9±0.3	9.9±0.1	6.3±0.1	9.9±0.2	9.5±0.3
PFOA	9.9±0.6	9.8±0.1	4.5±0.1	10.0±0.4	9.9±0.5	10.0±0.4	10.0±0.9	8.9±0.3	7.0±0.1	9.5±0.8
PFHpA	8.0±0.2	7.6±0.1	8.7±0.8	10.0±0.4	10.0±0.7	3.0±0.1	3.1±0.1	2.9±0.1	7.1±0.2	9.9±0.9
PFHxA	2.9±0.1	2.6±0.1	7.3±2.1	10.0±0.1	3.0±0.2	4.9±0.6	4.9±0.1	2.9±0.1	7.5±0.3	1.9±0.7
PFPeA	2.0±0.2	*no ads*	3.9±4.4	10.0±0.1	9.9±0.9	1.5±0.1	*no ads*	5.6±0.4	5.8±0.2	7.2±0.4
PFBA	*no ads*	*no ads*	3.8±2.5	8.9±0.1	6.8±0.3	*no ads*	*no ads*	2.5±0.9	6.8±0.1	6.0±0.4
PFOS	4.5±0.6	7.8±0.1	9.9±0.1	10.0±0.1	9.8±0.1	9.9±0.9	9.9±0.9	9.9±0.1	9.9±0.3	9.9±0.1
PFHxS	1.1±0.1	2.1±0.1	9.9±0.1	10.0±0.3	10.0±0.9	3.9±0.9	9.7±0.1	9.0±2.5	7.9±0.4	9.2±0.7
PFBS	0.4±0.1	*no ads*	*n/m*	8.4±2.1	6.7±0.3	1.2±0.9	*no ads*	*n/m*	2.1±0.1	3.4±0.3
PFOSA	9.4±0.4	9.0±0.3	*n/m*	9.4±0.5	8.8±1.3	8.0±0.4	8.3±0.1	*n/m*	6.7±0.3	8.4±1.0
PFOSaAm	8.8±0.8	9.9±0.1	9.9±0.1	6.7±0.6	9.3±1.0	9.9±0.2	10.0±0.4	9.3±0.1	5.9±0.1	8.0±0.3

Table S6. r^2 values (coefficient of determination) for second order kinetics linear regression fits,

PFAS	r^2									
	ionic strength = 0 mM					ionic strength = 50 mM				
	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC
PFDA	0.999	0.999	0.989	0.998	0.994	0.999	0.995	0.999	0.997	0.995
PFNA	0.989	0.965	0.999	0.986	0.994	0.999	0.999	0.999	0.998	0.997
PFOA	0.999	0.999	0.997	0.995	0.993	0.999	0.999	0.997	0.999	0.980
PFHpA	0.999	0.999	0.975	0.996	0.991	0.999	0.999	0.999	0.997	0.976
PFHxA	0.998	0.999	0.804	0.999	0.982	0.994	0.998	0.998	0.993	0.963
PFPeA	0.998	*no ads*	0.203	0.998	0.979	0.999	*no ads*	0.975	0.996	0.988
PFBA	*no ads*	*no ads*	0.999	0.999	0.995	*no ads*	*no ads*	0.999	0.999	0.987
PFOS	0.999	0.999	0.999	0.999	0.986	0.999	fast	0.999	0.999	0.999
PFHxS	0.999	0.999	0.999	0.995	0.989	0.999	0.999	0.999	0.991	0.981
PFBS	0.996	*no ads*	*n/m*	0.134	0.809	0.999	*no ads*	*n/m*	0.987	0.976
PFOSA	0.999	0.997	*n/m*	0.999	0.942	0.999	0.999	0.999	0.995	0.960
PFOSaAm	0.994	0.996	fast	0.977	0.968	0.999	0.993	0.999	0.999	0.996

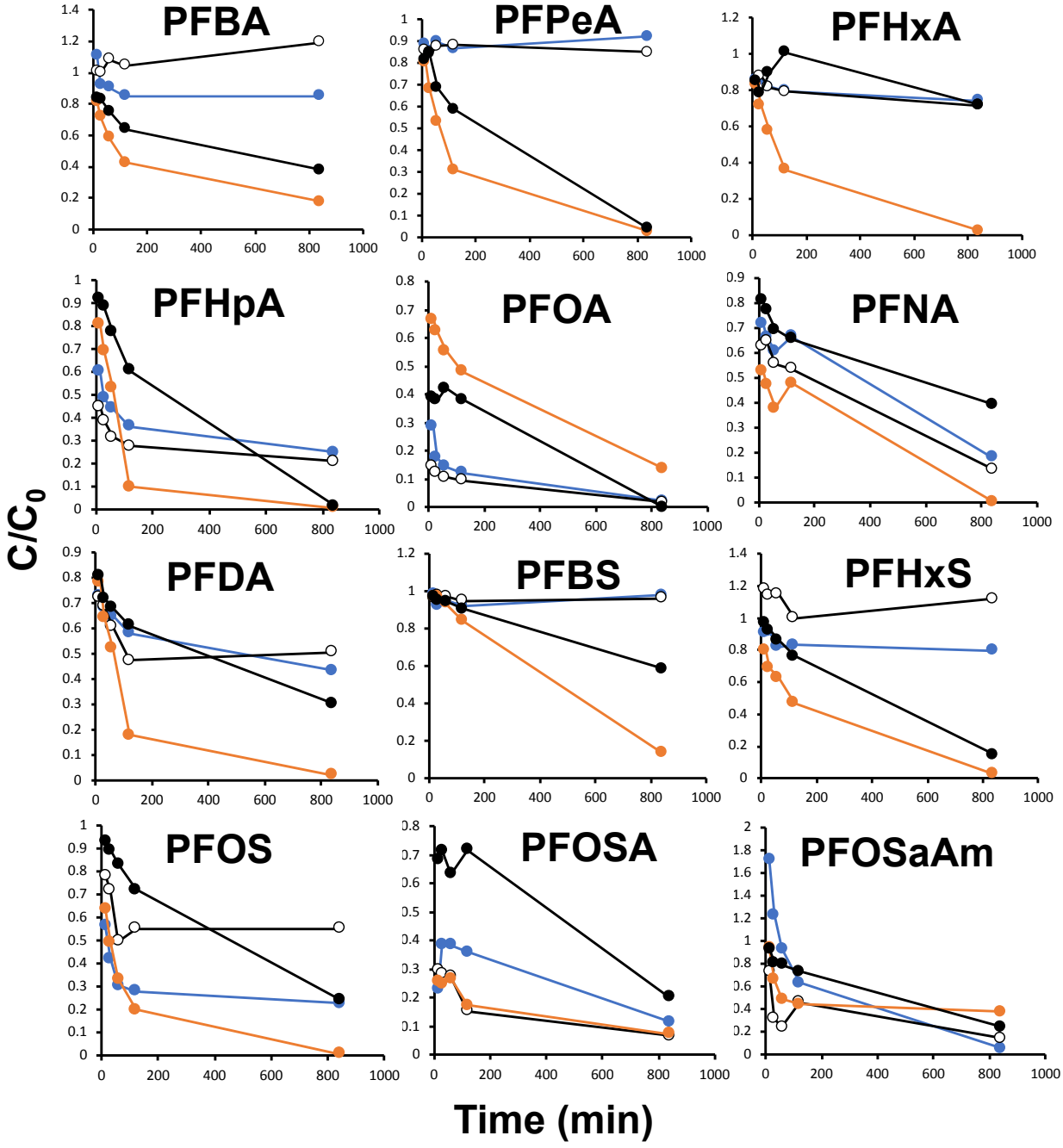

Figure S3a: Adsorption kinetics for SOMS (○); F-SOMS (ᔓ); poly-SOMS (ᔓ); and GAC (ᔓ). Dosage 200 mg/L, temperature 25°C, constant agitation, DI water.

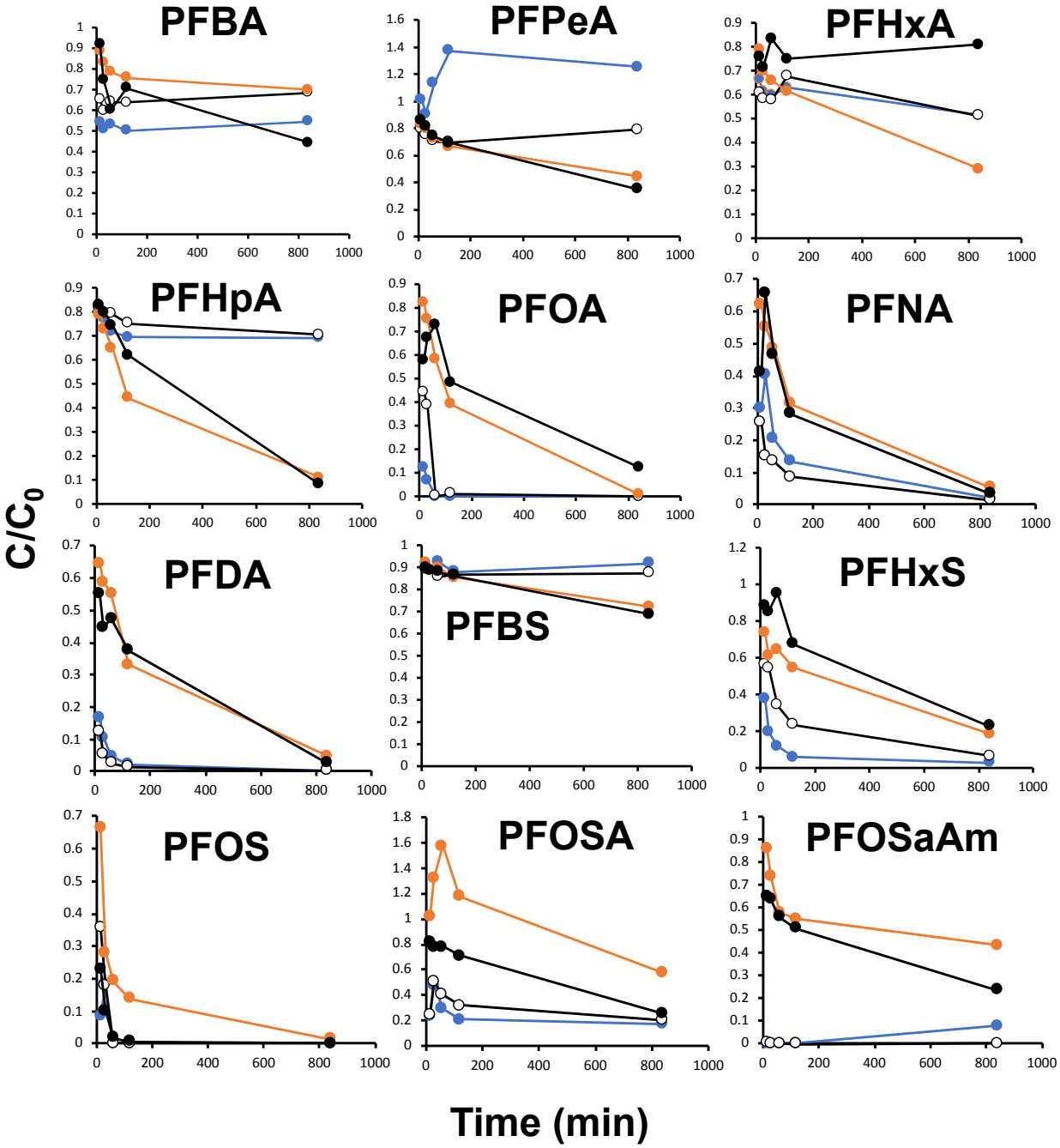

Figure S3b: Adsorption kinetics for SOMS (○); F-SOMS (ᔓ); poly-SOMS (ᔓ); and GAC (ᔓ). Dosage 200 mg/L, temperature 25°C, constant agitation, 50 mM NaCl.

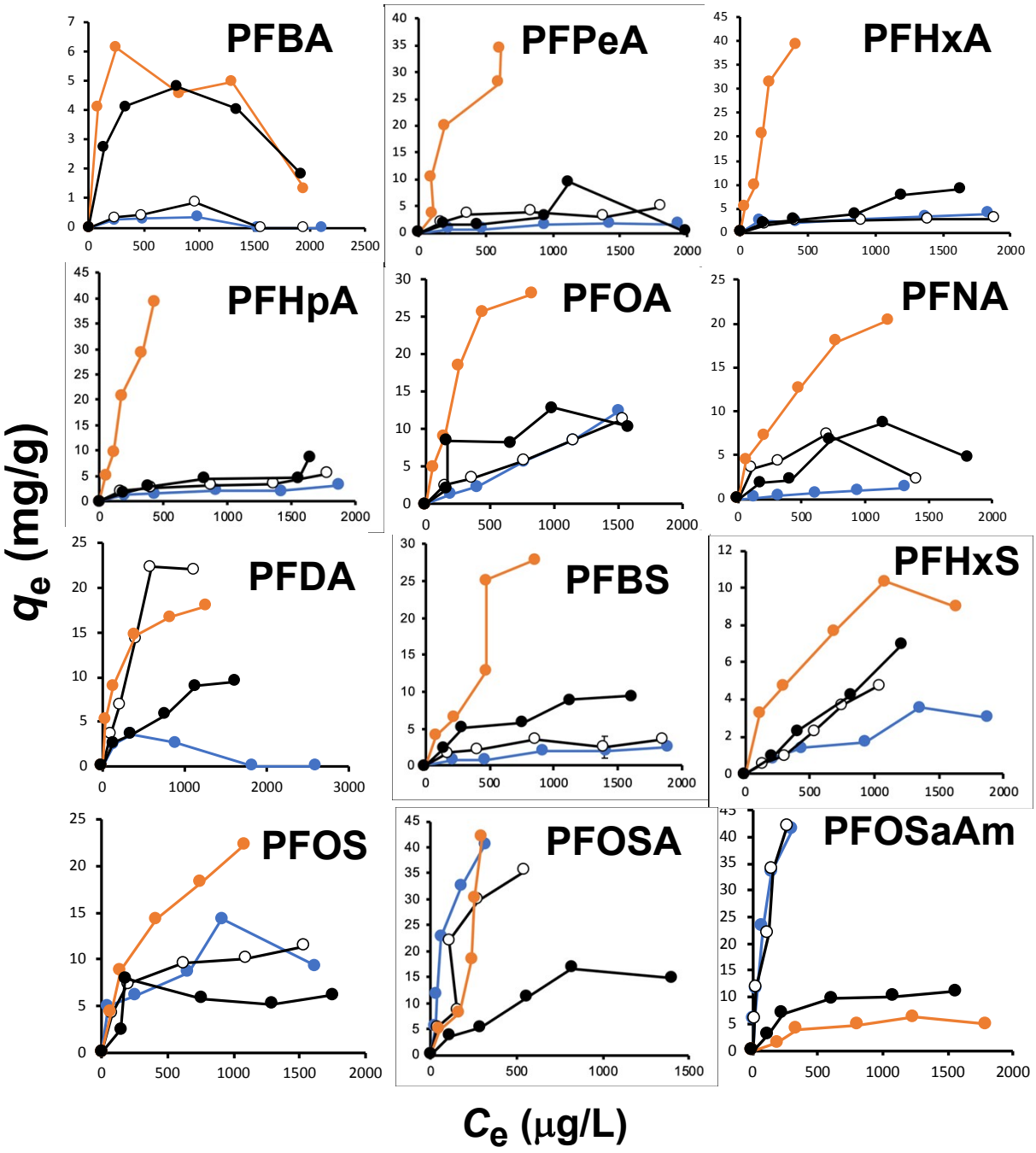

Figure S4a: Adsorption isotherms for SOMS (○); F-SOMS (ᘐ); poly-SOMS (ᘐ); and GAC (ᘐ). Dosage 40 mg/L, temperature 25°C, constant agitation, DI water.

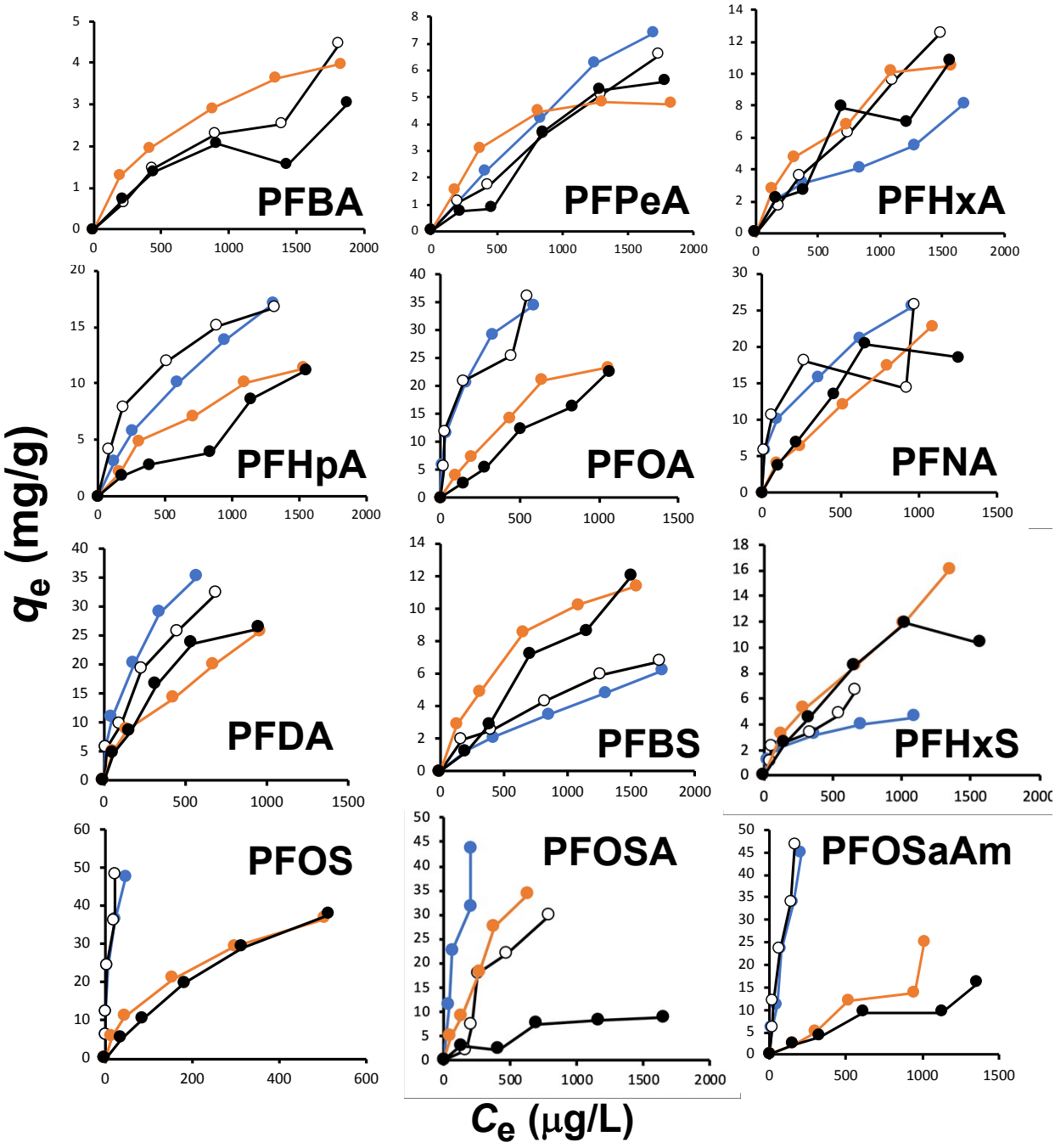

Figure S4b: Adsorption isotherms for SOMS (○); F-SOMS (ஜ); poly-SOMS (ஜ); and GAC (ஜ). Dosage 40 mg/L, temperature 25°C, constant agitation, 50 mM NaCl.

Table S7a: Freundlich constants and capacity for PFAS solutes in DI water.

PFAS Solute	Adsorbent	1/*n*	K_F (mg/g)(L/μg)$^{1/n}$	r^2	Capacity q_e (mg/g) at C_e = 200 μg/L
PFDA	SOMS	0.84±0.13	80±60	0.929	**6.8±0.8**
	F-SOMS	nominal adsorption			**0.1±0.1**
	poly-SOMS	0.37±0.04	1400±300	0.971	**10.0±0.2**
	GAC	0.56±0.07	150±60	0.961	**2.9±0.4**
PFNA	SOMS	does not fit Freundlich model*			**3.6±0.6**
	F-SOMS	nominal adsorption			**0.1±0.1**
	poly-SOMS	0.56±0.03	400±90	0.986	**7.7±0.2**
	GAC	0.60±0.26	79±35	0.640	**2.0±1.3**
PFOA	SOMS	0.65±0.07	85±40	0.966	**2.7±0.5**
	F-SOMS	1.12±0.06	3±1	0.991	**1.2±0.5**
	poly-SOMS	0.69±0.09	325±170	0.949	**12.7±0.5**
	GAC	0.84±0.08	30±16	0.971	**2.7±0.6**
PFHpA	SOMS	0.36±0.08	300±150	0.874	**2.0±0.6**
	F-SOMS	0.35±0.08	190±105	0.856	**1.2±0.7**
	poly-SOMS	0.92±0.08	145±40	0.976	**19.5±0.4**
	GAC	0.74±0.05	34±10	0.992	**1.7±0.3**
PFHxA	SOMS	0.23±0.04	540±150	0.900	**1.8±0.3**
	F-SOMS	0.19±0.09	820±480	0.605	**2.3±0.6**
	poly-SOMS	0.8±0.1	270±180	0.876	**22.8±0.6**
	GAC	0.7±0.1	45±40	0.890	**1.8±1.0**
PFPeA	SOMS	0.35±0.08	370±200	0.889	**2.3±0.6**
	F-SOMS	0.46±0.13	50±45	0.803	**0.6±1.4**
	poly-SOMS	0.55±0.10	960±550	0.937	**17.5±0.6**
	GAC	does not fit Freundlich model*			**1.3±0.9**
PFBA	SOMS	nominal adsorption			**0**
	F-SOMS	nominal adsorption			**0**
	poly-SOMS	does not fit Freundlich model**			**5.7±0.7**
	GAC	does not fit Freundlich model**			**3.2±0.5**
PFOS	SOMS	0.31±0.05	1180±370	0.927	**6.3±0.3**
	F-SOMS	0.19±0.02	2300±360	0.996	**6.4±0.2**
	poly-SOMS	0.57±0.06	430±160	0.972	**8.9±0.4**
	GAC	0.36±0.07	430±190	0.900	**2.9±0.5**
PFHxS	SOMS	1.13±0.10	2±1	0.979	**0.7±0.9**
	F-SOMS	0.64±0.12	25±20	0.902	**0.8±1.1**
	poly-SOMS	0.43±0.07	420±180	0.935	**4.2±0.4**
	GAC	1.11±0.07	3±1	0.999	**2.9±0.5**
PFBS	SOMS	0.28±0.11	425±300	0.691	**1.8±0.8**
	F-SOMS	0.62±0.15	25±20	0.847	**0.6±1.6**
	poly-SOMS	0.87±0.19	95±00	0.879	**7.7±1.1**
	GAC	0.53±0.10	210±130	0.905	**3.3±0.6**
PFOSA	SOMS	0.69±0.25	480±620	0.713	**19.1±1.3**
	F-SOMS	0.69±0.15	895±610	0.870	**34.9±0.7**
	poly-SOMS	2.86±0.38	<1	0.965	**13.1±2.1**
	GAC	0.64±0.12	160±120	0.905	**5.1±0.8**
PFOSaAm	SOMS	0.68±0.07	960±310	0.966	**35.5±0.3**
	F-SOMS	0.64±0.06	1260±320	0.974	**36.7±0.2**
	poly-SOMS	0.53±0.18	120±150	0.726	**2.0±1.3**
	GAC	0.45±0.12	440±330	0.831	**4.9±0.8**

Initial concentrations: 250, 500, 1000, 1500, 2000 ppb *q_e when C_e at 200 ppb calculated from isotherm. ** $q_e$when C_e at 200 ppb calculated from Freundlich fit of first three data points.

Table S7b: Freundlich constants and capacity for PFAS solutes in DI water.

PFAS Solute	Adsorbent	1/*n*	K_F (mg/g)(L/μg)$^{1/n}$	r^2	Capacity q_e (mg/g) at C_e = 200 μg/L
PFDA	SOMS	0.49±0.05	1260±350	0.957	**16.8±0.3**
	F-SOMS	0.51±0.01	1440±80	0.998	**21.2±0.1**
	poly-SOMS	0.56±0.03	510±80	0.992	**10.1±0.2**
	GAC	0.67±0.07	300±110	0.971	**10.6±0.4**
PFNA	SOMS	0.28±0.08	3060±1300	0.813	**13.6±0.4**
	F-SOMS	0.36±0.02	1930±180	0.994	**13.7±0.1**
	poly-SOMS	0.71±0.05	150±50	0.983	**6.4±0.3**
	GAC	0.70±0.10	165±120	0.913	**6.7±0.7**
PFOA	SOMS	0.44±0.10	2020±980	0.871	**21.2±0.1**
	F-SOMS	0.44±0.03	2190±290	0.989	**22.6±0.1**
	poly-SOMS	0.77±0.06	130±50	0.980	**7.4±0.4**
	GAC	1.06±0.06	15±5	0.989	**3.9±0.4**
PFHpA	SOMS	0.49±0.05	520±160	0.970	**7.1±0.3**
	F-SOMS	0.72±0.02	100±10	0.997	**4.5±0.1**
	poly-SOMS	0.70±0.09	70±37	0.956	**2.9±0.6**
	GAC	0.82±0.15	22±20	0.905	**1.7±1.1**
PFHxA	SOMS	0.93±0.03	14±3	0.999	**1.9±0.2**
	F-SOMS	0.52±0.07	150±70	0.942	**2.3±0.5**
	poly-SOMS	0.55±0.05	185±50	0.979	**3.5±0.3**
	GAC	0.72±0.20	50±55	0.863	**2.3±1.1**
PFPeA	SOMS	0.87±0.05	10±3	0.999	**1.0±0.4**
	F-SOMS	0.91±0.03	9±2	0.996	**1.1±0.3**
	poly-SOMS	0.49±0.10	140±100	0.877	**1.9±0.7**
	GAC	1.12±0.20	2±2	0.892	**0.5±2.5**
PFBA	SOMS	nominal adsorption			**0**
	F-SOMS	nominal adsorption			**0**
	poly-SOMS	0.51±0.02	85±10	0.996	**1.3±0.2**
	GAC	0.54±0.15	45±40	0.804	**0.8±1.4**
PFOS	SOMS*	0.44±0.07	11000±9700	0.991	**>56.0±0.2**
	F-SOMS**	0.47±0.07	8600±1340	0.943	**>68.0±0.2**
	poly-SOMS	0.52±0.01	1450±90	0.998	**23.4±0.1**
	GAC	0.76±0.03	355±50	0.995	**19.7±0.2**
PFHxS	SOMS	0.52±0.12	190±130	0.855	**3.0±0.7**
	F-SOMS	0.35±0.02	400±50	0.988	**2.7±0.1**
	poly-SOMS	0.66±0.04	130±30	0.991	**4.2±0.2**
	GAC	0.66±0.11	100±60	0.988	**3.3±0.7**
PFBS	SOMS	0.57±0.05	95±35	0.973	**2.0±0.4**
	F-SOMS	0.74±0.01	25±2	0.999	**1.2±0.1**
	poly-SOMS	0.58±0.05	170±50	0.980	**3.8±0.3**
	GAC	1.12±0.11	3±2	0.973	**1.3±0.8**
PFOSA	SOMS	1.42±0.50	3±9	0.721	**5.8±2.9**
	F-SOMS	0.63±0.17	1310±1000	0.875	**38.0±0.8**
	poly-SOMS	0.79±0.06	294±70	0.952	**14.3±0.3**
	GAC	0.51±0.22	200±280	0.643	**3.0±1.5**
PFOSaAm	SOMS	0.83±0.11	640±280	0.954	**52.6±0.4**
	F-SOMS	0.75±0.08	780±270	0.966	**41.9±0.4**
	poly-SOMS	1.09±0.16	11±8	0.943	**3.6±1.0**
	GAC	0.82±0.12	40±30	0.935	**2.9±0.8**

Initial concentrations: 250, 500, 1000, 1500, 2000 ppb *q_e at 200 ppb is outside the isotherm, extrapolation leads to q_e = 115.8 mg/g for PFOS to SOMS. **q_e at 200 ppb is outside the isotherm, extrapolation leads to q_e = 102.0 mg/g for PFOS to F-SOMS.

Table S8: Physical characteristics and PFOS adsorption capacity of F-SOMS adsorbents with variable amounts of fluoroalkyl composition.

Percent Mole Composition of Fluoroalkyl Precursor 2	BET Surface Area (m^2/g)	Pore Volume (mL/g)	Swell (mL/g)	q_e, PFOS (mg/g)*
0	646	1.03	7.6	16
7	621	0.80	7.0	18
13	660	1.04	6.6	17
19	500	0.60	6.3	10
31	420	0.54	6.2	15
47	283	0.50	6.0	7.5

* Measured by batch equilibrium adsorption initial concentration PFOS = 1000 μg/L, adsorbent dosage = 40 mg/L, equilibrium time = 20 h. q_e = 25 mg/g if PFOS was 100% adsorbed.

Table S9: Effluent concentration for PFOA and PFOS from columns (C_0 = 2,000 ng/L)

Applied Bed Volumes	Effluent Concentration (ng/L)				
	PFOA		PFOS		
	SOMS DI Water	F-SOMS DI Water	SOMS DI Water	SOMS 50 mM NaCl	F-SOMS DI Water
1000	69	88	42	21	29
2000	180	88	84	124	21
4000	370	74	91	58	62
6000	117	76	129	73	207

Error +/- 15% Flow: 0.5 bed volumes per minute.

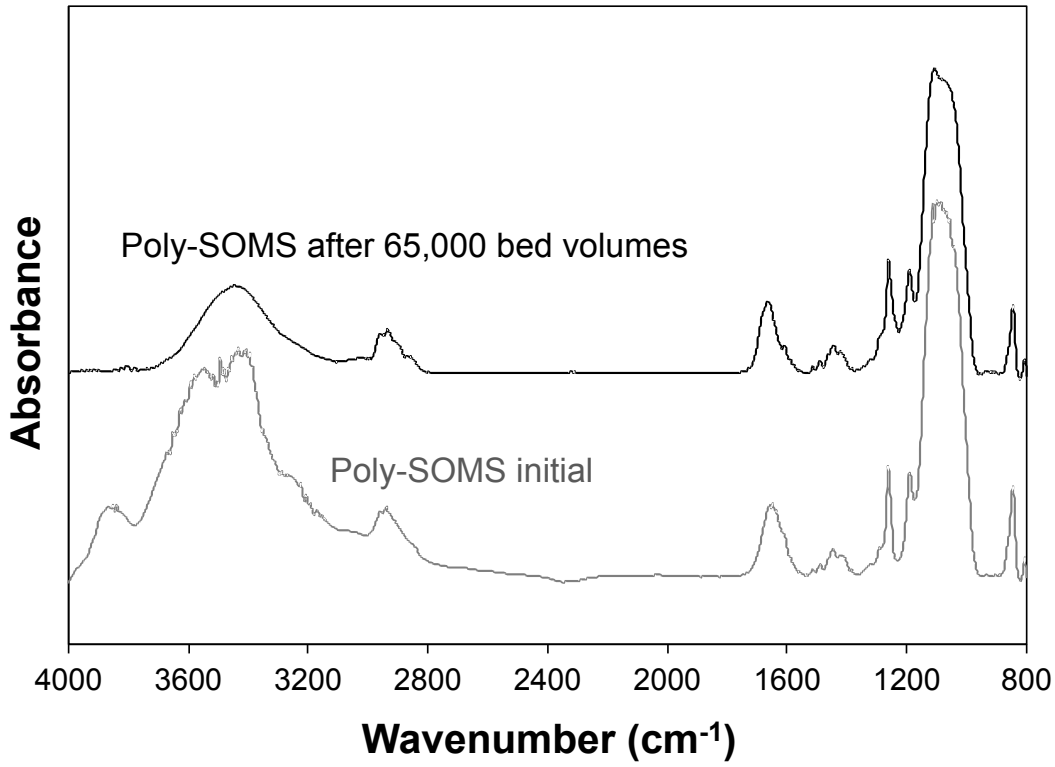

Figure S5: FT-IR spectra (KBr pellet) of poly-SOMS before and after use in column experiment with 12 component mixture of 200 μg/L PFAS compounds in DI water. 65,000 bed volumes of the PFAS solution had been passed through the poly-SOMS bed after which the material was dried at 25°C and measured by FT-IR. The amide band at 1650 cm^{-1} was used for quantitation.

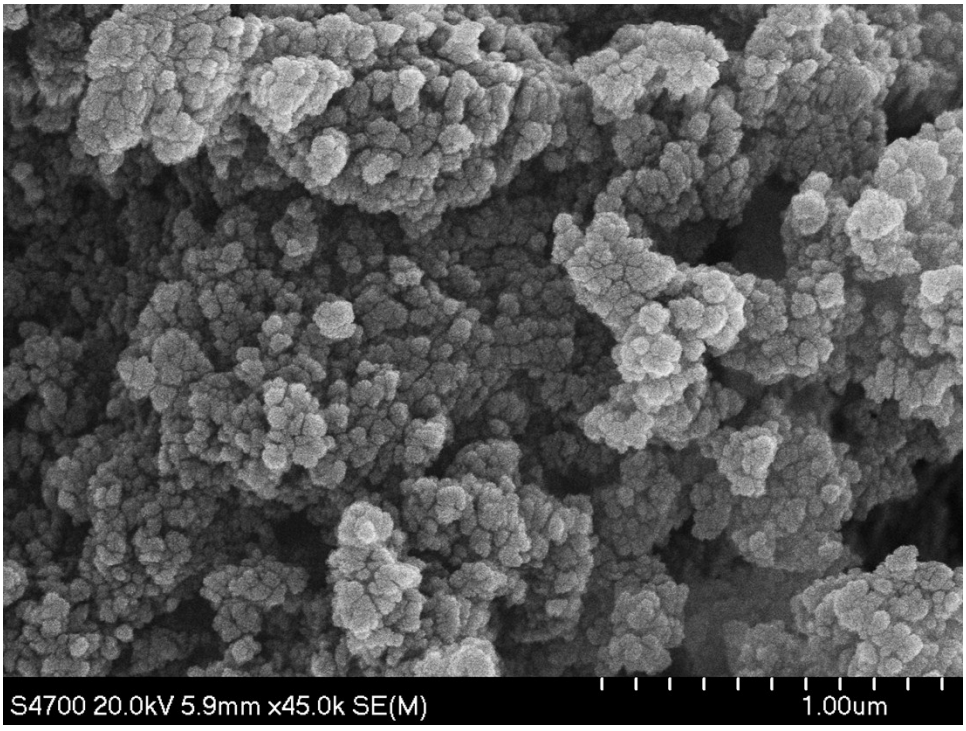

Figure S6. High resolution scanning electron microscopy image of SOMS interior pore structure.