Supporting Information

Adsorption of Perfluorocarboxylic Acids at the Silica Surface

Umer Shafique,[a,b] Vivien Dorn,[b] Albrecht Paschke,[a] Gerrit Schüürmann,*[a,b]

Experiments were carried out in 50 mL polypropylene (PE) Erlenmeyer flasks containing 0.1–2.0 g silica and 50 mL aqueous solution of PFCAs (in µmoles). Control solutions without silica were analyzed with each batch to account for the concentration loss due to sorption on container walls.

Table S1. Details of chemicals and reagents.

Name	**Abbreviation**	**CAS No.**	**Company**	**Physical State**
Perfluorooctanoic acid	PFOA	335-67-1	Sigma-Aldrich ®	Solid (96%)
Perfluorononanoic acid	PFNA	375-95-1	Sigma-Aldrich ®	Solid (97%)
Perfluorodecanoic acid	PFDA	335-76-2	Sigma-Aldrich ®	Solid (98%)
Perfluoroundecanoic acid	PFUnDA	34598-33-9	Sigma-Aldrich ® (Fluka)	Solid (95%)
Perfluorododecanoic acid	PFDoDA	307-55-1	Sigma-Aldrich ®	Solid (95%)
Iso-butanol	-	78-83-1	Sigma-Aldrich ®	Liquid (≥ 99%)
Isobutyl chloroformate	IBCF	543-27-1	Sigma-Aldrich ®	Liquid (98%)
Pyridine	-	110-86-1	Sigma-Aldrich ®	Liquid (99.8%)
Buffer pH 2.5	-	Indigenous (adjusting phosphoric acid pH with NaOH)		Liquid
Hexane	-	110-54-3	Sigma-Aldrich ®	Liquid (≥ 97%)
Acetonitrile	-	75-05-8	Sigma-Aldrich ®	Liquid (≥ 99.8%)
Methanol	-	67-56-1	Sigma-Aldrich ®	Liquid (≥ 99%)
Double-distilled water	-	-	Indigenous	Liquid

Table S2. LOD, retention times, molar masses, and highest mass fragments of selected PFCAs.

PFCA	Molar Mass	LOD (μmol L^{-1})	Retention Time (min)	Highest Mass Fragment *
PFOA	414.07	0.12	6.47	455
PFNA	464.08	0.11	7.09	505
PFDA	514.08	0.23	7.51	555
PFUnDA	564.09	0.34	7.87	605
PFDoDA	614.10	0.39	8.23	655

* highest mass fragments of corresponding isobutyl ester

Fig. S1. Operating conditions of GC EI MS.

Injection: 1 µl, split less, 250^{O}C

GC: Agilent, 7890A

Column: Agilent, HP5-MS, 30 m × 0.25 mm × 0.25 µm

MS: Agilent, 5975C, m/z = 69, 131, 169, 181, 250^{O}C

Flow gas: He, Pressure: 56.07 kPa, Flow rate: 1.1 ml min^{-1}

Oven Program

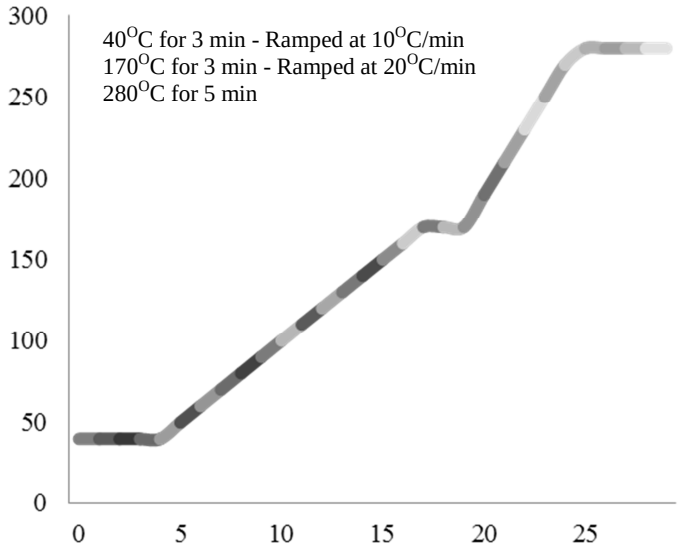


Fig. S2. Analytical Procedure.

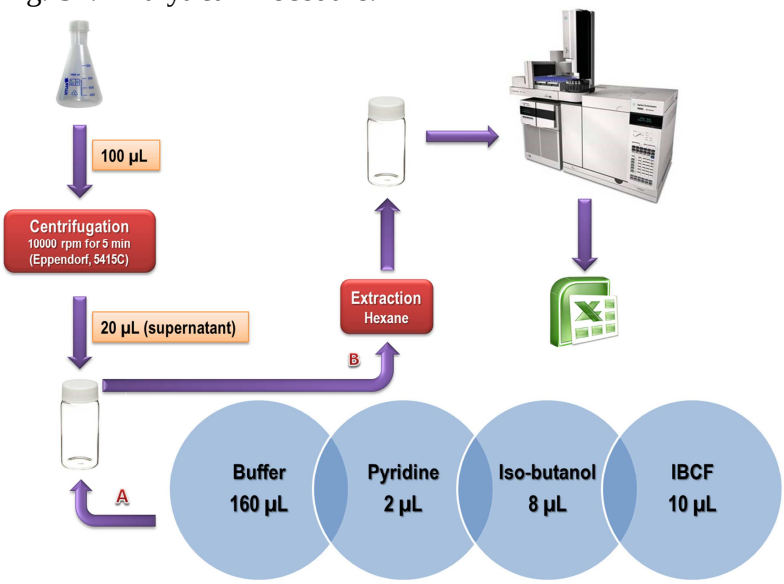


Fig. S3. The percentage decrease in aqueous concentration of PFCAs during storage in glass containers (initial concentration 25 µmol L^{-1}, volume 0.01 L, room temperature, glass bottles were filled up to maximum and closed with steel lids containing rubber).

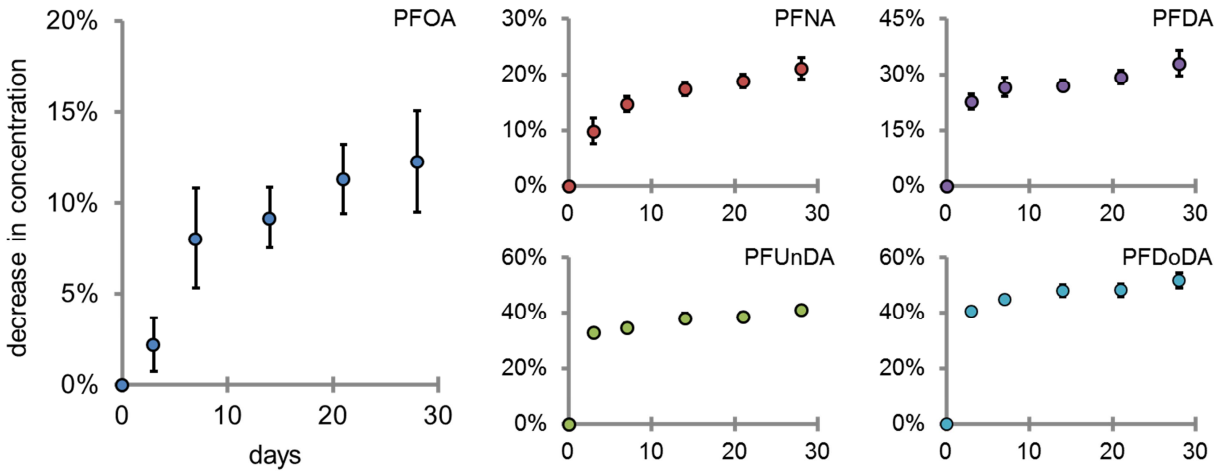


Fig. S4. Surface of silica.

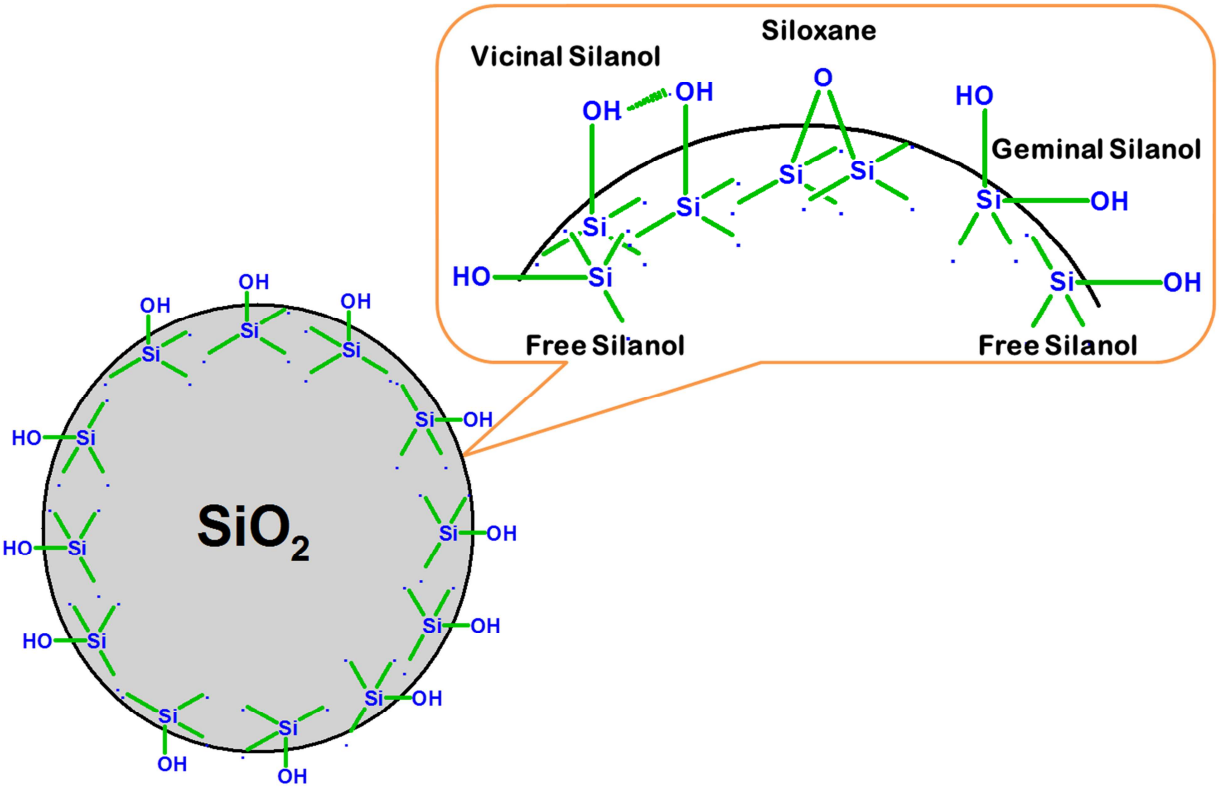
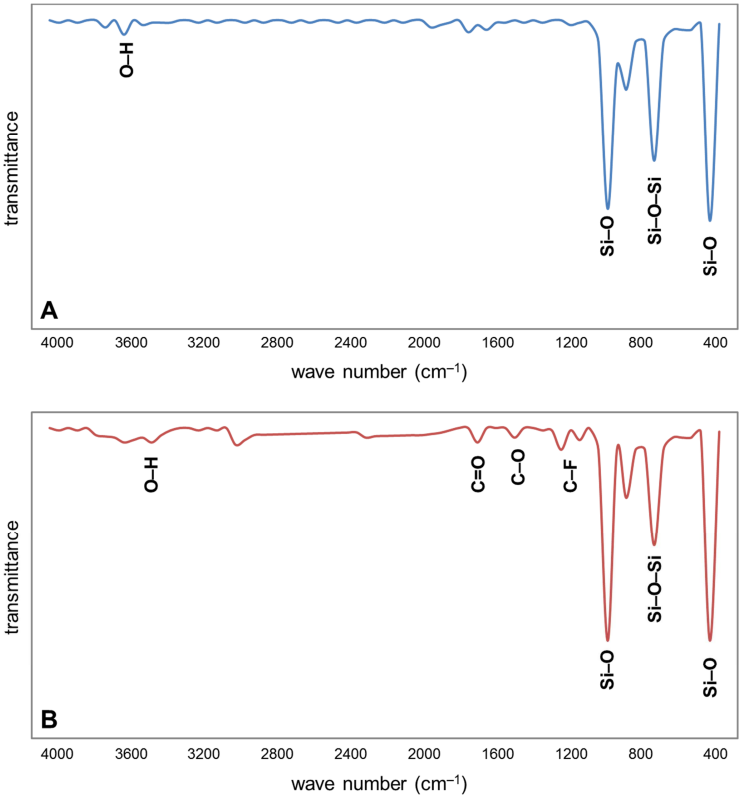


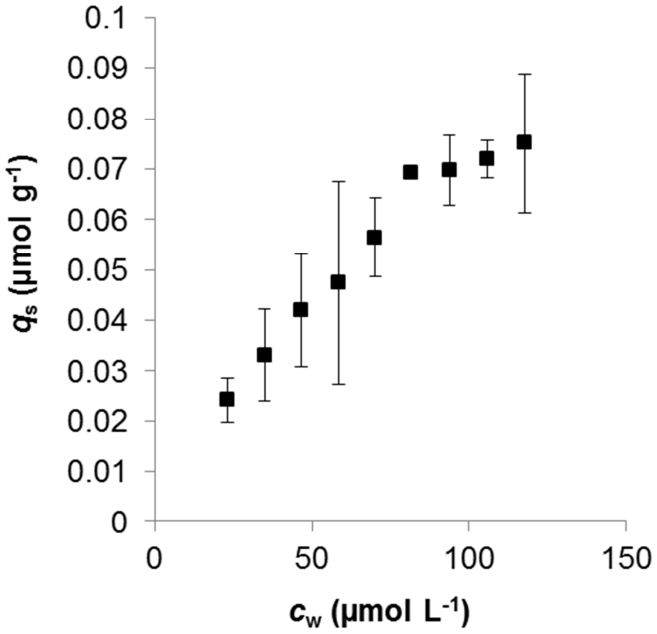
Fig. S5. ATR–FTIR (attenuated total reflection-Fourier transform infrared) spectrum of the silica before (A) and after (B) adsorption of PFOA. [a]



[a] The IR absorption bands are as follows (from left to right): Si–O 460 cm^{-1} (rocking vibration 440–460 cm^{-1}); Si–O–Si 750 cm^{-1} (stretching vibration 740–760 cm^{-1}); Si–O 1060 cm^{-1} (asymmetric stretching vibration 950–1250 cm^{-1}); C–F 1250, 1140 cm^{-1} (symmetric and asymmetric stretching vibration 1000–1350 cm^{-1}); C–O 1450 cm^{-1} (symmetric stretching vibration 1390–1450 cm^{-1}); [also can be O–H 1450 cm^{-1} (deformation vibration 1390–1450 cm^{-1})]; C=O 1715 cm^{-1} (symmetric stretching vibration 1680–1740 cm^{-1}); (Si–)O–H 3610 cm^{-1} (bending vibration 3580–3670 cm^{-1}; hydrogen bonded O–H band is broad when measuring for (RCO–)O–H (3400–2500 cm^{-1}).

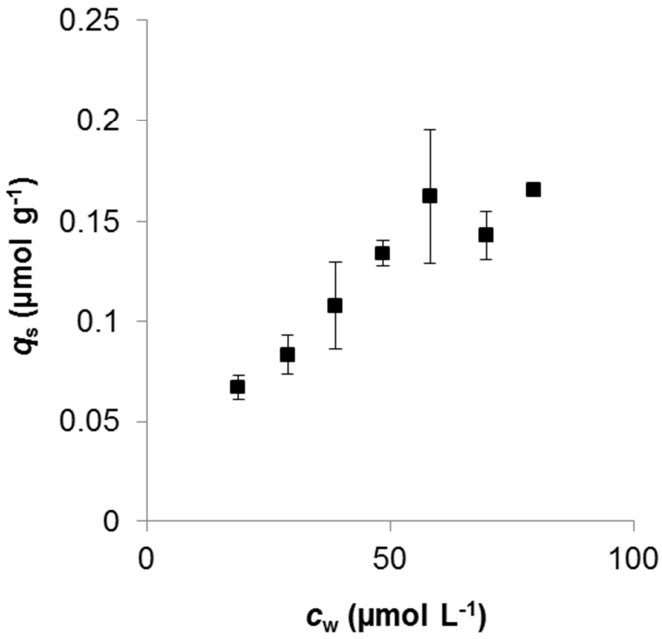
Note: For B, acidic pH conditions and high PFOA aqueous concentration were employed because no significant PFOA-related absorption band was observed under normal conditions. Interestingly, the proposed mechanism for the PFOA adsorption at the silica or glass surface can be understood as being similar to that at the air-water interface. Therefore, a way forward toward a definitive proof – triggered by and going beyond the present study – would be to investigate or model silica in the aqueous phase. Our presently proposed mechanism has been derived from judiciously designed batch experiments and a thermodynamic evaluation of temperature-dependent findings.

Fig. S6. Adsorption of PFOA at the silica surface.



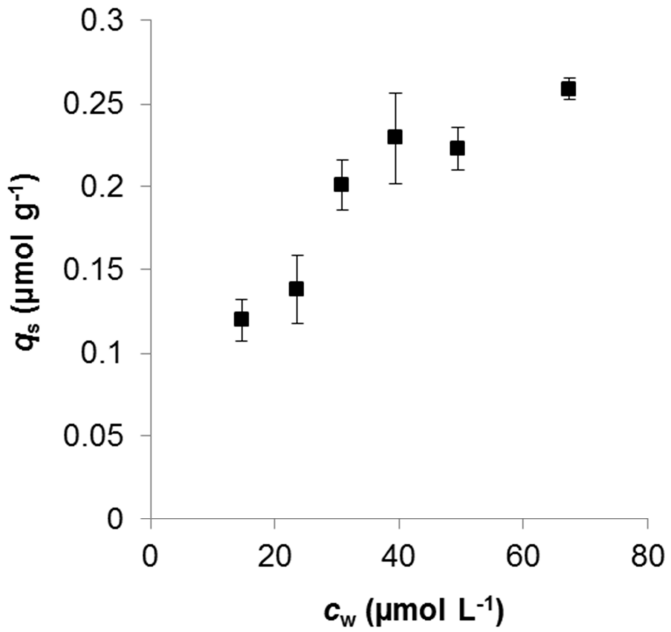
Experimental conditions: PFOA 20–125 µmoles L^{-1}, solution volume 0.05 L, silica 1.0 g, BET surface area 480.4 m^2 g^{-1}, pH 5.0, no background electrolyte, temperature 298.15 K.

Fig. S7. Adsorption of PFNA at the silica surface.



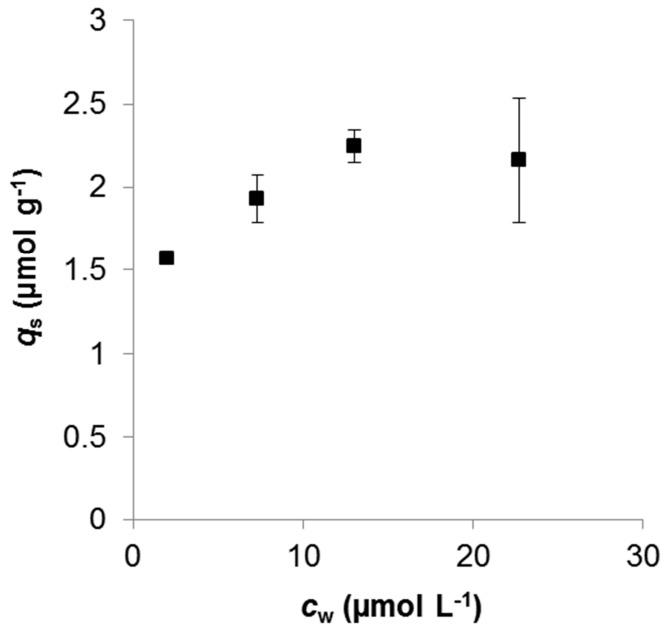
Experimental conditions: PFNA 20–90 µmoles L^{-1}, solution volume 0.05 L, silica 1.0 g, BET surface area 480.4 m^2 g^{-1}, pH 5.0, no background electrolyte, temperature 298.15 K.

Fig. S8. Adsorption of PFDA at the silica surface.



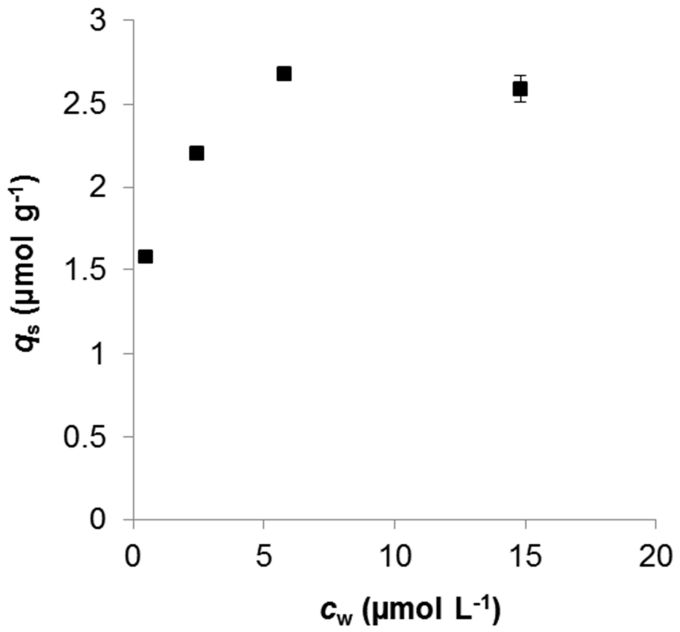
Experimental conditions: PFDA 20–75 µmoles L^{-1}, solution volume 0.05 L, silica 1.0 g, BET surface area 480.4 m^2 g^{-1}, pH 5.0, no background electrolyte, temperature 298.15 K.

Fig. S9. Adsorption of PFUnDA at the silica surface.



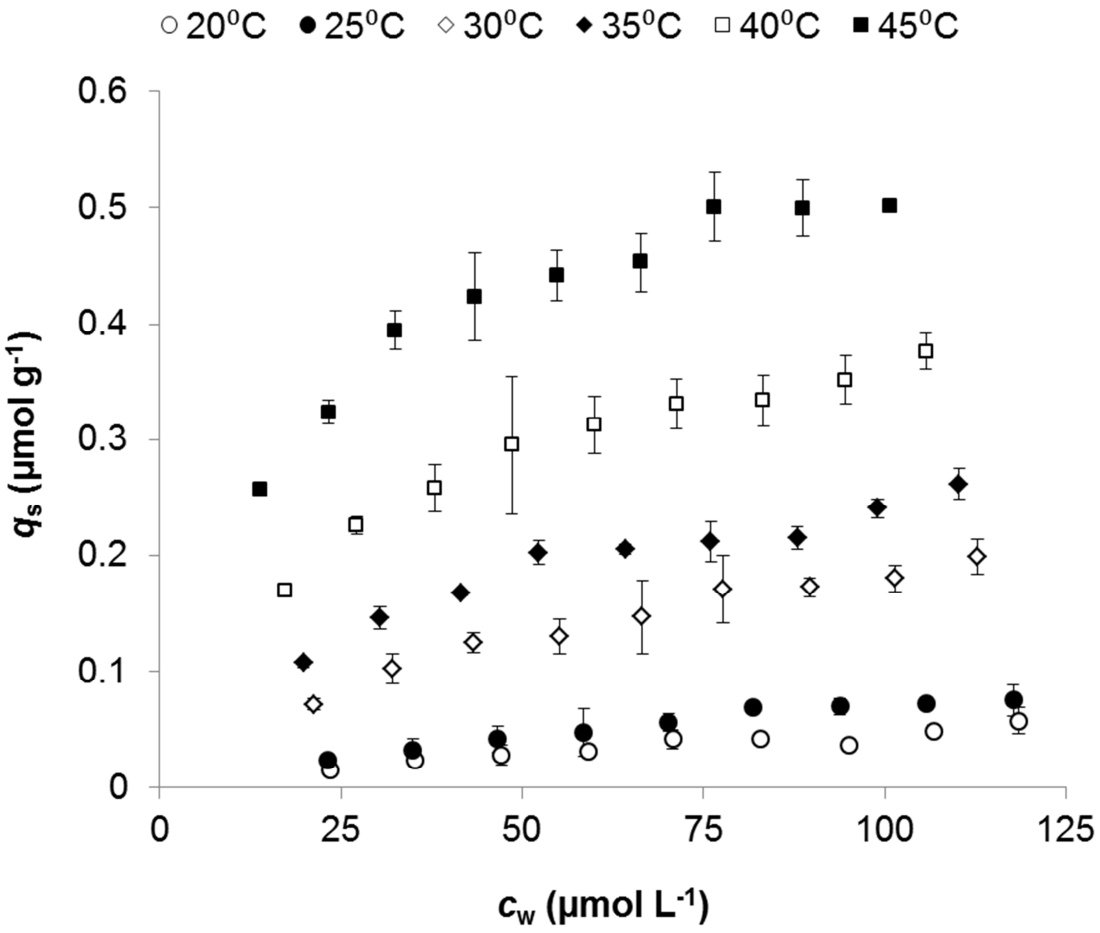
Experimental conditions: PFUnDA 15–45 µmoles L^{-1}, solution volume 0.05 L, silica 0.5 g, BET surface area 480.4 m^2 g^{-1}, pH 5.3, no background electrolyte, temperature 298.15 K.

Fig. S10. Adsorption of PFDoDA at the silica surface.



Experimental conditions: PFDoDA 15–40 µmoles L^{-1}, solution volume 0.05 L, silica 0.5 g, BET surface area 480.4 m^2 g^{-1}, pH 5.3, no background electrolyte, temperature 298.15 K.

Fig. S11. Effect of temperature on adsorption of PFOA at the silica surface.



Experimental conditions: PFOA 20–125 µmoles L^{-1}, solution volume 0.05 L, silica 1.0 g, BET surface area 480.4 m^2 g^{-1}, pH 5.0, no background electrolyte, temperature 293.15–318.15 K.

Fig. S12. Van 't Hoff plot for adsorption of PFOA at the silica surface.

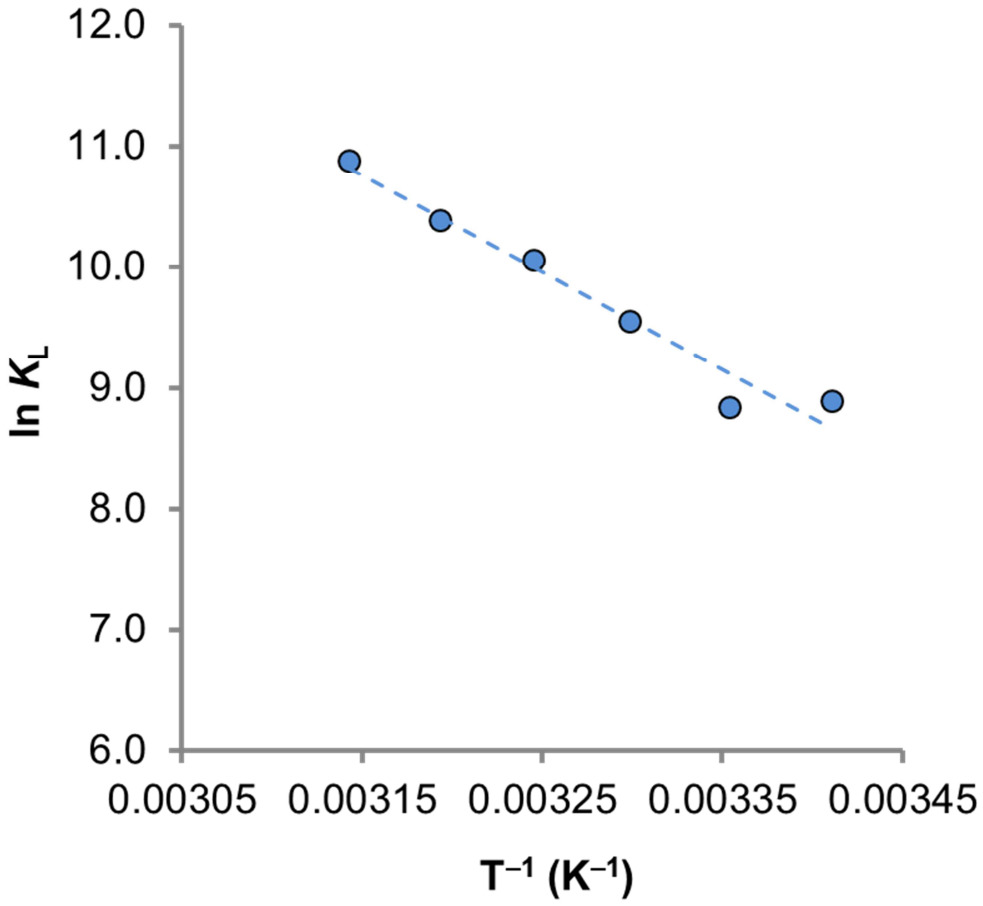
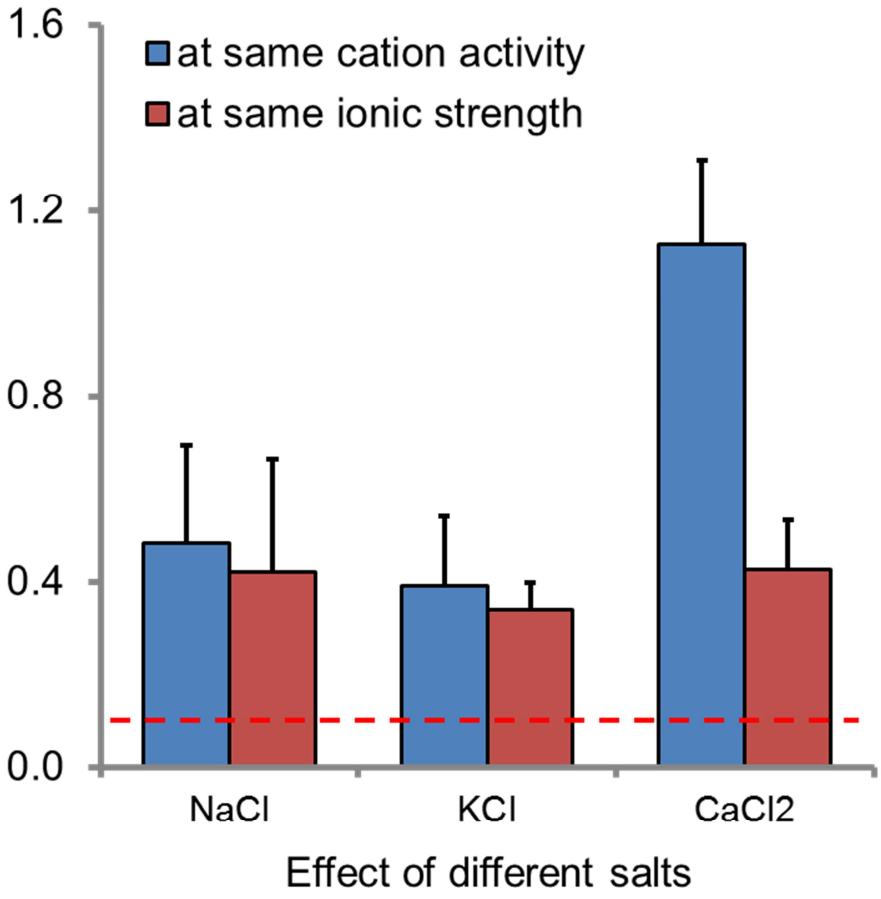


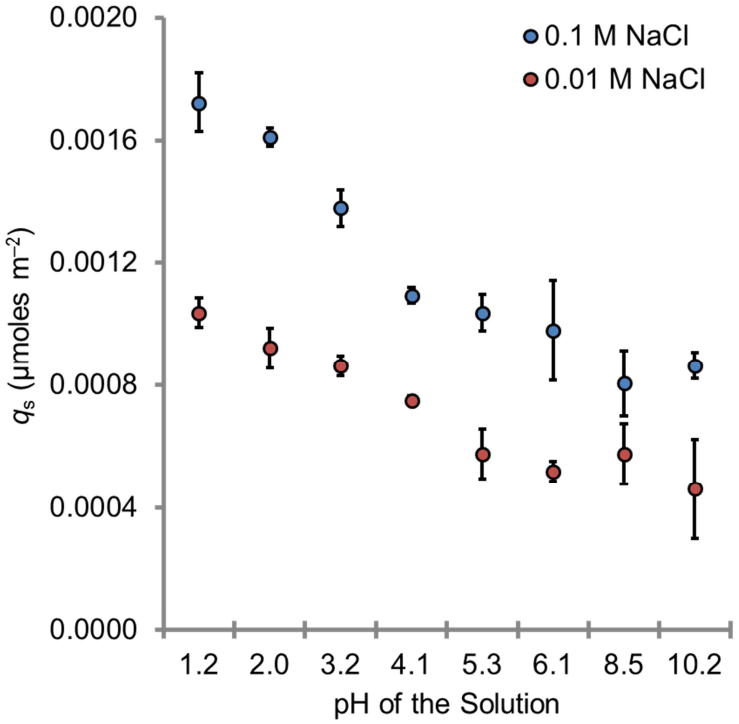
Fig. S13. Effect of cations of background electrolyte on PFOA adsorption at the silica surface.



Experimental conditions: PFOA 125 μmoles L^{-1}, solution volume 0.05 L, silica 1.0 g, BET surface area 480.4 m^2 g^{-1}, pH 5.0, temperature 298.15 K.

Note: Red dotted line shows adsorption of PFOA at the silica surface in absence of salt in the solution.

Fig. S14. PFOA adsorption at the silica surface at different pH and ionic strength.



Experimental conditions: PFOA 125 µmoles L^{-1}, solution volume 0.05 L, silica 1.0 g, BET surface area 480.4 m^2 g^{-1}, temperature 298.15 K.