Supporting Information

Rapid Destruction and Defluorination of Perfluorooctane Sulfonate by Alkaline Hydrothermal Reaction

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Table S1. Reagent List.

Reagent	Purity grade	CAS#	Supplier
PFASs			
Perfluorooctanesulfonate (PFOS)	40 wt.% in water	1763-23-1	Sigma-Aldrich, USA
Perfluorooctanoic acid (PFOA)	95%	335-67-1	Sigma-Aldrich, USA
Perfluoroheptanoic acid (PFHpA)	>99%	375-85-9	Wellington Laboratories, Canada
Perfluorohexanoic acid (PFHxA)	>99%	307-24-4	Wellington Laboratories, Canada
Perfluoropentanoic acid (PFPeA)	>99%	2706-90-3	Wellington Laboratories, Canada
Perfluorobutanoic acid (PFBA)	>99%	375-22-4	Wellington Laboratories, Canada
Isotopically labeled internal standards			
[$^{13}C_4$]PFOS	>99%	Not available	Wellington Laboratories, Canada
[$^{13}C_4$]PFOA	>99%	Not available	Wellington Laboratories, Canada
[$^{13}C_4$]PFHpA	>99%	Not available	Wellington Laboratories, Canada
[$^{13}C_2$]PFHxA	>99%	Not available	Wellington Laboratories, Canada
[$^{13}C_5$]PFPeA	>99%	Not available	Wellington Laboratories, Canada
[$^{13}C_4$]PFBA	>99%	Not available	Wellington Laboratories, Canada
Bases and Acids			
NaOH	97%	1310-73-2	Merck, Germany
$Ca(OH)_2$	95%	1305-62-0	Sigma-Aldrich, USA
Na_2CO_3	99.5%	497-19-8	Sigma-Aldrich, USA
HCl	30 wt.% in water	7647-01-0	Sigma-Aldrich, USA
H_2SO_4	98%	7664-93-9	Sigma-Aldrich, USA
HNO_3	65 wt.% in water	7697-37-2	Sigma-Aldrich, USA
Oxidants			
K_2FeO_4	97%	39469-86-8	Element 26 Technol, TX, USA
$KMnO_4$	97%	7722-64-7	Sigma-Aldrich, USA
K_2CrO_4	99%	9016-11-9	Sigma-Aldrich, USA
$NaClO_4$	98%	7601-89-0	Sigma-Aldrich, USA
$NaClO_3$	97%	7775-09-9	Sigma-Aldrich, USA
NaClO	Available chlorine: 5 wt. % in water	7681-52-9	Sigma-Aldrich, USA
H_2O_2	30 wt.% in water	7722-84-1	Sigma-Aldrich, USA
Reductants			
$NaBH_4$	98%	16940-66-2	Sigma-Aldrich, USA
Na_2SO_3	98%	7757-83-7	Sigma-Aldrich, USA
$Na_2S_2O_3$	99.5%	7772-98-7	Sigma-Aldrich, USA
$Na_2S_2O_4$	82.5%	7775-14-6	Sigma-Aldrich, USA
$Na_2S_2O_5$	98%	7681-57-4	Sigma-Aldrich, USA
$Na_2S_2O_8$	98%	7775-27-1	Sigma-Aldrich, USA
$NaHSO_5$	98%	28831-12-1	Sigma-Aldrich, USA
KI	99%	7681-11-0	Sigma-Aldrich, USA
$FeSO_4$	99%	7782-63-0	Sigma-Aldrich, USA
Fe(0)	97%, 325 mesh	7439-89-6	Sigma-Aldrich, USA
Other			
$NaNO_3$	99%	7631-99-4	Sigma-Aldrich, USA
$FeCl_3$	97%	7705-08-0	Sigma-Aldrich, USA
$NiCl_2$	98%	7718-54-9	Sigma-Aldrich, USA
$ZnCl_2$	97%	7646-85-7	Sigma-Aldrich, USA
NaH_2PO_4	99%	7558-80-7	Sigma-Aldrich, USA
Na_2HPO_4	99%	7558-79-4	Sigma-Aldrich, USA
NaF	99%	7681-49-4	Sigma-Aldrich, USA
D_2O	99.96 atom % D	7789-20-0	Sigma-Aldrich, USA
Octanoic acid	99%	124-07-2	Sigma-Aldrich, USA
Ammonium acetate	Optima LC-MS grade	631-61-8	Fisher Scientific, USA
Ammonium hydroxide	Optima grade	1336-21-6	Fisher Scientific, USA
Methanol	Optima LC-MS grade	67-56-1	Fisher Scientific, USA
Isopropanol	Optima LC-MS grade	67-63-0	Fisher Scientific, USA
Water (for LC-MS/MS)	Optima LC-MS grade	7732-18-5	Fisher Scientific, USA

Text S1. Preparation of nanoscale Fe, Ni and Zn particles

Nanoscale Fe(0), Ni(0) and Zn(0) particles used in the amendment screening experiment were prepared following procedures previously reported.[1-3] Briefly, a 1.6 mol·L^{-1} $NaBH_4$ aqueous solution was added dropwise to a continuously stirred solution containing either 1 mol·L^{-1} $FeCl_3$, $NiCl_2$ or $ZnCl_2$ under a reducing atmosphere (glovebox filled with 98% N_2 and 2% H_2). The dissolved metal ions were reduced according to the following reactions:

$$2\ Fe^{3+} + 6\ BH_4^- + 18\ H_2O = 2\ Fe(0)(s) + 6\ B(OH)_3 + 21\ H_2 \quad (s1)$$

$$Ni^{2+} + 2\ BH_4^- + 6\ H_2O = Ni(0)(s) + 2\ B(OH)_3 + 7\ H_2 \quad (s2)$$

$$Zn^{2+} + 2\ BH_4^- + 6\ H_2O = Zn(0)(s) + 2\ B(OH)_3 + 7\ H_2 \quad (s3)$$

The resulting metal precipitates were allowed to settle out of solution before washing and drying with acetone inside the glovebox.

Text S2. Reaction procedure

Stock solutions of PFOS and PFOA (500 mg/L) as well as aqueous reactive amendments (typically 1.11 mol/L) were prepared in deionized water (Milli-Q system). Using the amendment stock solution to dilute PFOS stock solution by 10 times could lead to a typical reaction system containing 50 mg·L^{-1} PFOS and 1 mol·L^{-1} amendment. Hydrothermal conversion experiments focused on identifying amendments that promote degradation of PFOS because initial tests showed that it was much more recalcitrant than perfluorooctanoic acid (PFOA). Whereas test reactions without any added amendments showed >99% degradation of 50 mg/L PFOA (250 °C, 30 min), <1% of PFOS degraded under the same conditions.

Batch hydrothermal reactions were conducted in duplicate using stainless steel mini-tube reactors plugged with Swagelok® stainless steel-316 port connectors on both ends (10 cm long, 1/2 in. outer diameter, 0.049 in. wall thickness, and 5.33 mL working volume). Amendment screening experiments were first conducted to examine PFOS degradation and defluorination in the presence of a wide range of acids, bases, oxidants, and reductants. An aqueous solution of PFOS (typically 50 mg/L; 0.001 mol/L) was added to the reactor together with the desired amendment (typically 1 mol/L) before sealing. The reactor was then placed into a temperature-controlled fluidized sand bath (TIPTEMP company, NJ, USA) that was preheated to the desired reaction temperature (200-350 °C). Separate tests with thermocouples inserted into the same reactors filled with water showed that the reactor temperature reached the target value within 4 min. After the specified reaction time passed, the reactor was removed from the sand bath and quickly cooled to room temperature by submerging in a container of tap water. Thermocouple readings also showed that reactor contents were cooled within 2 min). The reactor was then opened, and liquid contents were collected for analysis.

Text S3. Analysis

A. Fluoride ion analysis

Fluoride ion concentrations were measured by fluorine ion selective electrode (Thermo Fisher, MA USA) after pH buffering of the samples to pH 5.0-5.5. The standard addition tests and ion chromatography (IC) analysis were conducted to verify the accuracy of fluoride ion measurement by electrode method. Fluoride was added into the reacted samples (50 mg·L^{-1} PFOS, 1 mol·L^{-1} NaOH; 350 °C, 90 min) as NaF, and the electrode-measured recovery rates of additional F^- ions were 110-115% as shown in Figure S1a. The electrode-measured fluoride ion concentration of time-course samples (50 mg·L^{-1} PFOS, 1 mol·L^{-1} NaOH; 350 °C, 0-480 min) was also in accordance with that of IC analysis (Figure S1b).

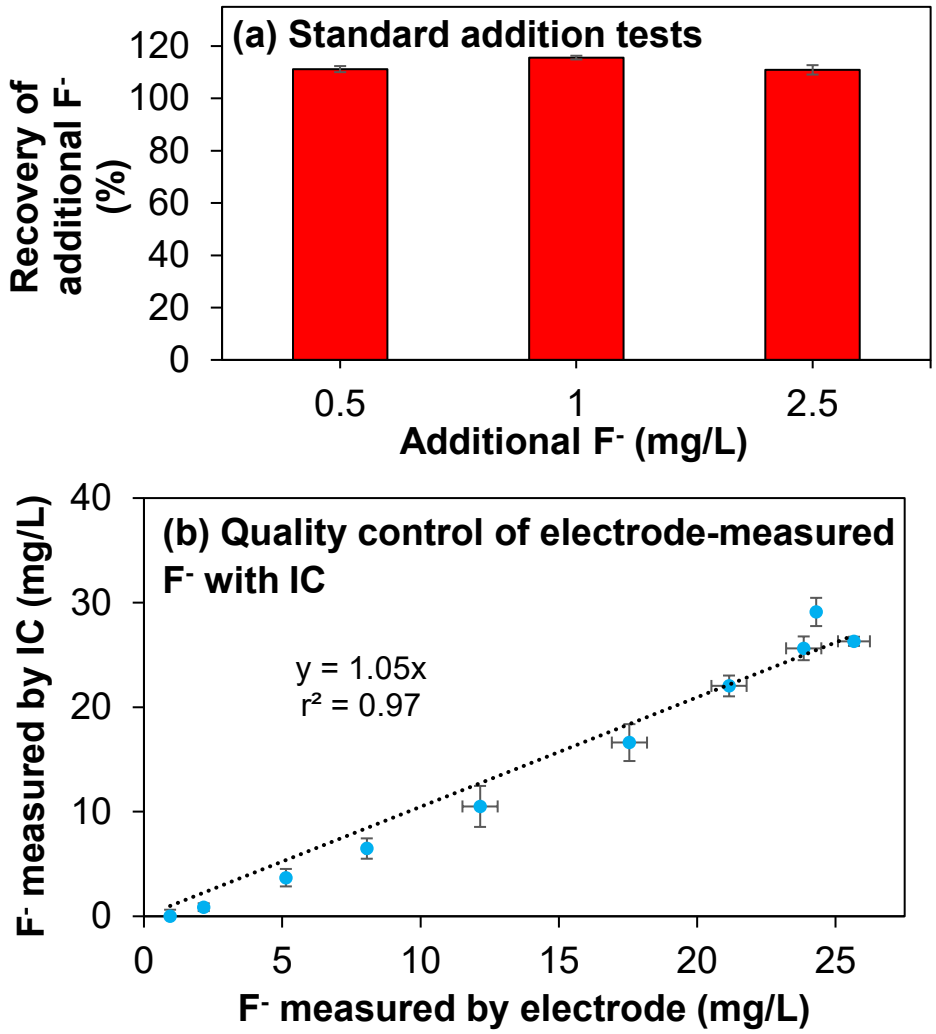

Figure S1. Accuracy evaluation of electrode measurement of fluoride ion concentration. (a) Electrode-measured recovery rates of additional fluoride ions added to the reacted samples (50 mg·L^{-1} PFOS, 1 mol·L^{-1} NaOH; 350 °C, 90 min). (b) Comparison of IC- and electrode-measured fluoride ion concentrations of reacted PFOS samples for different reaction time periods. Each symbol represents one sample collected at a certain reaction time. The higher yield of fluoride ion was due to the longer reaction time. Reaction conditions: PFOS (50 mg/L), NaOH (1 mol/L), 350 °C, 0-480 min. Error bars represent min/max values observed for duplicate experiments (smaller than symbol if not visible).

B. LC-MS/MS analysis

Concentrations of PFOS and selective perfluoroalkyl acid intermediate products were determined by liquid chromatography coupled with triple quadrupole mass spectrometry (LC-MS/MS; Agilent 1100 LC coupled to an Applied Biosystem API 3200 triple-quad mass spectrometer). Prior to analysis, samples were diluted 100,000-fold with a solution containing isotopically labeled internal standards (Table S1), methanol, isopropanol, and dilute ammonium hydroxide. Chromatographic separations of the injected samples (1 mL) were performed using a Phenomenex (Torrance, CA, USA) Gemini C18 (100 × 3 mm, 5 µm) analytical column, which was preceded by a Phenomenex Gemini C18 guard column (4 × 2 mm) and two Agilent (Santa Clara, CA, USA) Zorbax Diol guard columns (4.6 × 12.5 mm, 6 µm). Analytical and guard columns were maintained at 40 °C during

analysis. Flow rate was 0.6 ml/min, and the gradient mobile phase consisted of 20 mM of Ammonium acetate in water (A) and in methanol (B) starting at 10% B, increased to 50% B in the first 0.5 min, increased to 99% B at 8 min, and maintained for 5 min, decreased to 10% B in 0.5 min, and maintained at 10% B to 20 min. Samples were introduced into the mass spectrometer via electrospray ionization (negative mode) with an applied voltage of -4500 V. Source temperature was 550 °C, spectra accumulation time was 0.2 s, and scan time was 0.842 s. Detailed MS/MS analysis condition is described in table S2.

Table S2. PFAS analytes names (acronyms), acquisition masses, parameters, internal standard used for LC-MS/MS analysis. Number next to analytes name represents selected for quantification (1) or confirmation (2).

Name (Acronym)	Precursor > Product ion	DP	EP	CE	CXP	IS
PFBA(1)	212.83 > 168.9	-10	-4.5	-12	0	MPFBA(1)
PFPeA(1)	262.84 > 218.9	-10	-5	-12	0	M5PFPeA(1)
PFHxA(1)	312.906 > 269	-10	-6	-12	0	M2PFHxA(1)
PFHxA(2)	312.906 > 118.8	-10	-6	-30	-4	M2PFHxA(1)
PFHpA(1)	362.9 > 319.1	-10	-4	-12	-2	M4PFHpA(1)
PFHpA(2)	362.9 > 168.9	-10	-4	-26	0	M4PFHpA(2)
PFOA(1)	412.912 > 369	-10	-4.5	-14	-2	M4PFOA(1)
PFOA(2)	412.912 > 168.9	-10	-4.5	-24	-4	M4PFOA(1)
PFOS(1)	498.897 > 79.9	-70	-7.5	-86	-6	MPFOS(1)
PFOS(2)	498.897 > 98.9	-70	-7.5	-54	0	MPFOS(1)
MPFBA(1)	216.859 > 171.8	-10	-4.5	-16	0	
M5PFPeA(1)	267.852 > 222.9	-10	-4	-12	-2	
M2PFHxA(1)	314.98 > 269.98	-10	-6	-12	-2	
M2PFHxA(2)	314.98 > 120	-10	-6	-30	0	
M4PFHpA(1)	366.898 > 322	-15	-5.5	-12	-2	
M4PFHpA(2)	366.898 > 171.9	-15	-5.5	-24	0	
M4PFOA(1)	416.929 > 372.1	-10	-4	-14	0	
M4PFOA(2)	416.929 > 171.9	-10	-4	-28	-4	
MPFOS(1)	502.968 > 79.9	-70	-7	-74	-6	
MPFOS(2)	502.968 > 98.9	-70	-7	-66	0	

1. Selected for Quantification; (2), selected for confirmation; DP, declustering potential; CE, collision energy; EP, entrance potential; CXP, collision cell exit potential; IS, used IS the native compound

C. Nuclear magnetic resonance (NMR) analysis

^{19}F NMR analysis of reacted PFOS solutions was used to verify the defluorination performance and to identify the chemical form of possible residual organic fluorine. In order to enhance the signal intensity, NMR analysis was performed on PFOS with an elevated concentration before and after hydrothermal reaction for different time periods. Reaction conditions were as follows: PFOS (5 mM, total fluorine = 85 mM), NaOH (1 mol/L), 350 ℃, 0-600 min. All the samples were diluted 50:50 in D_2O before collecting spectra. ^{19}F spectra were recorded at 500 MHz on a JEOL ECA-500 spectrometer. 128 scans were obtained in 13107 data points over a spectral window from -200 ppm to 200 ppm (0.544 s acquisition time) using a 30° flip-angle pulse with ^{1}H decoupling. The ^{19}F 90° pulse width was 8.5 μs. A 10 s relaxation delay was employed. The free induction decays (FIDs) were processed using exponential multiplication (line-broadening 1 Hz) before Fourier transformation.

D. HPLC analysis

Concentrations of octanoic acid, the un-fluorinated analogue of PFOA were determined by high performance liquid chromatography (HPLC; Agilent 1200 HPLC coupled to differential refraction index (RID) detector). The chromatographic separations of the injected samples (50 µL) were performed using a Spherisorb ODS2 Column (80Å, 5 µm, 4.6 mm X 250 mm, 1/pkg). The flow rate was 1 mL/min, and the mobile phase consisted of H_2SO_4 in HPLC water (pH 2.4, 2 mL 1N H_2SO_4 in 500 mL HPLC water) (A, 40%) and acetonitrile (B, 60%). The elution time for octanoic acid was 20 min.

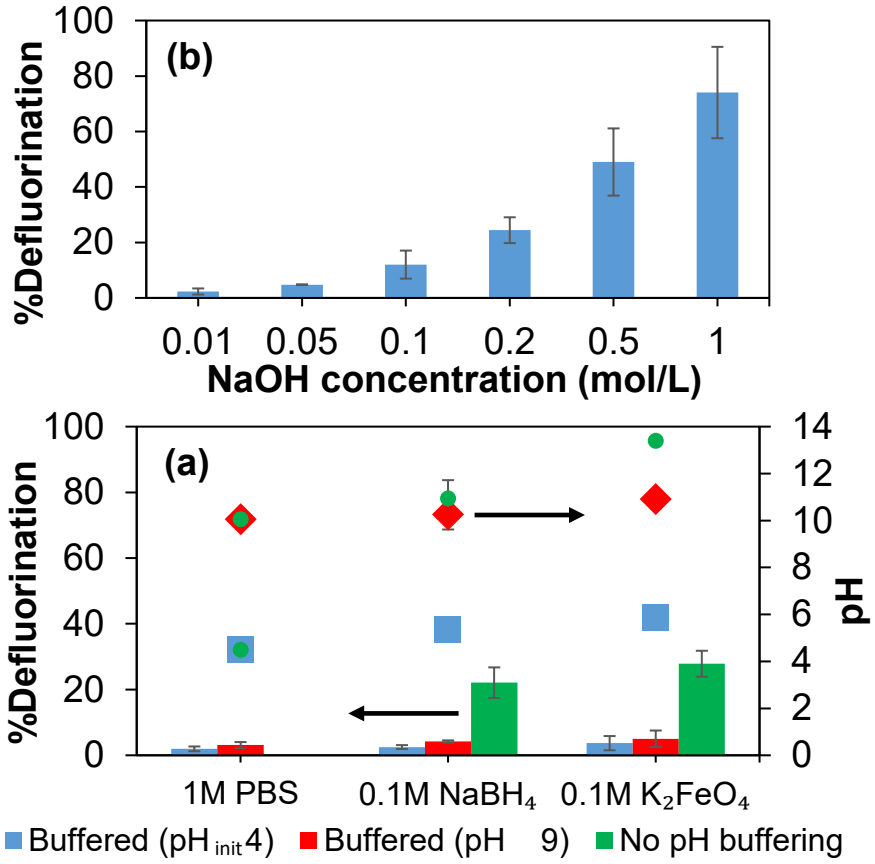

Figure S2. Effect of NaOH concentration and the pH of solutions amended with other reagents on hydrothermal defluorination of PFOS. (a) Extent of PFOS defluorination observed following 90 min reaction (350 °C) in water amended with varying NaOH concentrations. (b) Extent of PFOS defluorination following 90 min reaction in water amended with either a strong reductant ($NaBH_4$) or strong oxidant (K_2FeO_4) where solutions are either unbuffered or buffered at pH 9 or 4 using phosphate (PBS, 1 mol/L). Bars indicate the extent of defluorination (left axis) and symbols represent the pH values measured after quenching the reactions. Error bars represent min/max values observed for duplicate experiments (smaller than symbol if not visible).

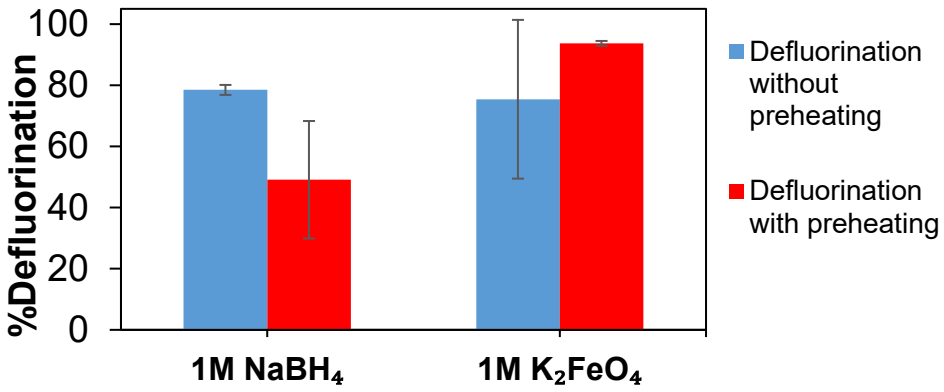

Figure S3. Effect of preheating (and re-cooling) solutions amended with $NaBH_4$ or K_2FeO_4 before introducing PFOS and re-heating on the extent of PFOS defluorination. Reaction conditions: 50 mg/L PFOS; Solutions pre-heated to 350°C for 90 min before re-cooling and introducing 50 mg/L PFOS and reacting at 350°C for another 90 min. Error bars represent min/max values observed for duplicate experiments.

Table S3. Measured Reaction Kinetics[a]

PFOS (mg/L)	NaOH (mol/L)	k_{obs} (min^{-1})	R^2	$k_{2,350°C}$ ($M^{-1}\cdot min^{-1}$)
50	1	0.015±0.001	0.95	0.052±0.004
	2.5	0.10±0.01	0.95	
	5	0.28±0.02	0.96	

[a]Reaction conditions: PFOS (50 mg/L) and NaOH amendment (1, 2.5 and 5 mol/L) in deionized water at 350 °C for 0-480 min. Uncertainties in k_{obs} values represent min/max values determined in duplicate experiments. Uncertainties in $k_{2,350°C}$ values represent the min/max values obtained by plotting k_{obs} values and NaOH concentrations.

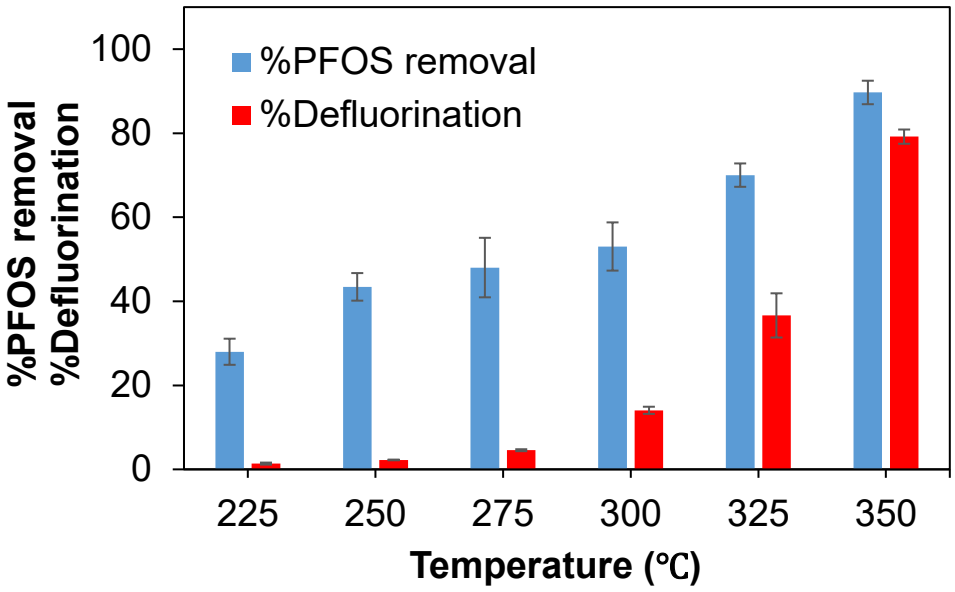

Figure S4. Effect of reaction temperature on the extent of PFOS degradation and defluorination in solutions amended with NaOH. Reaction conditions: PFOS (50 mg/L), NaOH (1 mol/L), 350 ℃, 90 min. Error bars represent min/max values observed for duplicate experiments.

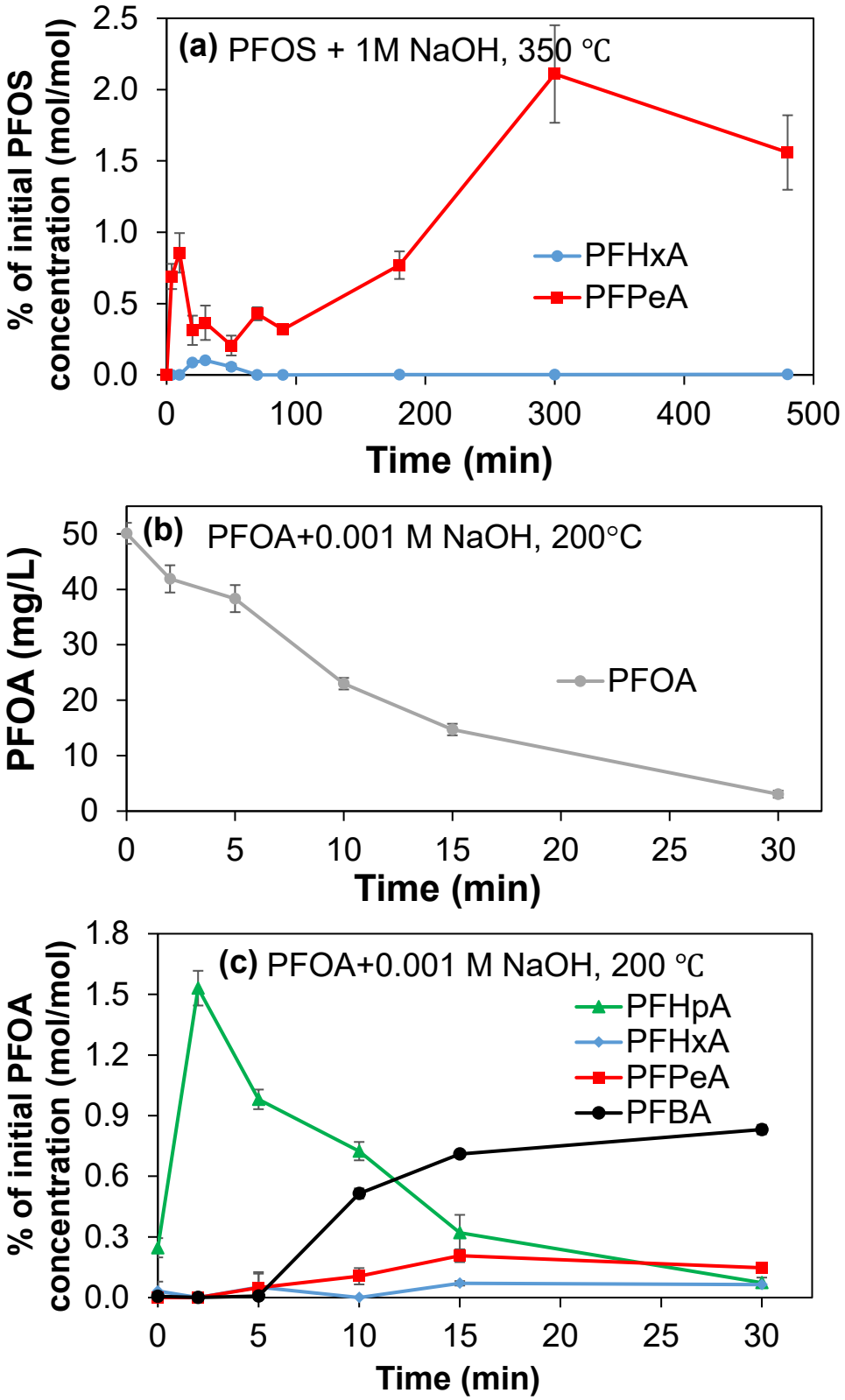

Figure S5. Intermediate products observed during hydrothermal treatment of (a) 50 mg/L PFOS with 1 M NaOH at 350 °C, (b, c) 50 mg/L PFOA with 0.001 M NaOH at 200 °C. Error bars represent min/max values observed for duplicate experiments (smaller than symbol if not visible).

References Cited in Supporting Information

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2. Cheng, R.; Zhou, W.; Wang, J.-L.; Qi, D.; Guo, L.; Zhang, W.-X.; Qian, Y., Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: role of nano-Ni and its size effect. *J. Hazard. Mater.* **2010,** *180*, 79-85.
3. Arnold, W. A.; Roberts, A. L., Pathways of chlorinated ethylene and chlorinated acetylene reaction with Zn (0). *Environ. Sci. Technol.* **1998,** *32*, 3017-3025.