# Supporting information for Biomimetic degradation of perfluorinated acids by vitamin $B_{12}$ with nano-zero-valent iron/nickel bimetal: Effects of their self-structure and coexisting substances

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**Text S1.** Sample pretreatment

The vials were removed from the orbital shaker regularly. The vials were opened to the atmosphere at least 30 min. The solution was transferred to 50-mL polypropylene (PP) centrifuge tubes. All tubes were centrifuged at 10615×g for 15 min (H1850R, Cence, Changsha, China). The supernatant was decanted to measure the pH values and fluoride concentrations, and the remaining supernatant was then transferred to a volumetric flask. The headspace vials were rinsed 3 times with 2 mL methanol followed by 10 mL 1% acetic acid solution (V/V) each time. The rinse medium was collected in the centrifuge tube, and centrifuged at 10615×g for 15 min. The supernatant was transferred to volumetric flask, and the residual solid in the centrifuge tube was sonication-assisted extracted 3 times with 2 mL methanol followed by 10 mL 1% acetic acid solution (V/V) each time. The extracts were also decanted to the volumetric flask after centrifugation with 10615×g. The collected supernatants were diluted with Milli-Q water to one tenth of the original sample concentration.

**Text S2.** The methods for solid-phase extraction

**The methods for Envi-C18 SPE cartridges**

Envi-C18 SPE cartridges were activated by 5 mL methanol, and equilibrated with 5 mL Milli-Q water. The cartridges were loaded with 5 mL sample solutions (adjust the pH to 2.5-3.0 with formic acid) at approximately 1 drop/s. The loaded cartridges were then washed with 5 mL of Milli-Q water, vacuum-dried for 1 hour, and eluted with 10 mL of methanol. The eluents were collected and transferred into a 10 mL PP centrifuge tubes.

**The methods for WAX cartridges**

WAX cartridges were activated by 10 mL 0.1% $NH_4OH$ in methanol and 10mL methanol sequentially, and equilibrated with 10 mL 1% acetic acid. The cartridges were loaded with 5 mL sample solutions (adjust the pH to 2.5-3.0 with formic acid) at approximately 1 drop/s. The loaded cartridges were then washed with 10 mL of 20% methanol-formic acid solution, vacuum-dried for 1 hour, and eluted with 10 mL of methanol containing 0.1% $NH_4OH$. The eluents were collected and transferred into a 10 mL PP centrifuge tubes.

**Text S3.** The methods analysis for PFCs and its products

**The methods for PFCs analysis via HPLC-MS/MS**

Concentrations of PFCs were analyzed by a high performance liquid chromatography – triple quadrupole mass spectrometry system (HPLC-MS/MS, Agilent 1260 HPLC, and AB Sciex 3500 MS). For HPLC separation, a 10 μL sample was loaded onto an Agilent Poroshell 120 EC-C18 column (2.7 μm, 3.0 mm×100mm) eluted with 250 μL/min of 10 mmol/L ammonium acetate (A) and methanol (B). The linear gradient was as follows: 80% A for 0-1 min, 25% A for 2-8 min, 5% A for 9-14 min, and 80% A for 14.01-18 min. The mass spectra were acquired under negative ionization (ESI) mode. The ion spray voltage was set to -4500 V, and the temperature was set to 550 ℃. The curtain gas, collision gas, ion source gas 1, and ion source gas 2 flow were set to 20, 8, 50, and 55 psi, respectively. The specific parameters of mass spectrometry of each PFCs were listed in Table S1.

**The products of PFCs analysis via UPLC-QTOF**

PFAS degradation products were measured by ultra-performance liquid chromatography-quadrupole time of flight mass spectrometry (UPLC-QTOF, Agilent 1290, and Agilent 6545). For UPLC separation, a 20 μL sample was loaded onto an Agilent ZORBAX RRHD Eclipse Plus C18 column (1.8 μm, 3.0 mm×100mm) eluted with 400 μL/min of 5 mmol/L ammonium acetate (A) and methanol (B). The linear gradient was the same as above described. The mass spectra were acquired under negative ionization (ESI) mode. The gas temperature and sheath gas temperature were set to 300 and 350 ℃. The nebulizer was set to 30 psi. The sheath gas flow was set to 10 L/min. The fragmentor and spray voltage were set to 120 and 4000V.

Potential degradation products were determined according to the following criteria. The

following regulations should be satisfied simultaneously, if the substance is present in the sample: (i) m/z difference errors ≤ ± 30 ppm; (ii) the abundance value of non-isotopic quasi molecular ions should be more than three times the abundance value of isotopic quasi molecular ions at the same time. In addition, if the peak area of a substance in the degraded sample is twice or more than that in the controls, the substance is considered to be a degradation product, and if it is less than twice but has a significant difference, it is considered to be a suspicious degradation product.

Table S1 Parameters of mass spectrometer

| PFCs | Parent ion | Quantitative | | Qualitative | | DP |
|---|---|---|---|---|---|---|
| | | Daughter ion | Collision energy (eV) | Daughter ion | Collision energy (eV) | |
| PFBA | 212.90 | 169.10 | -13.68 | - | - | -17.95 |
| PFHpA | 363.20 | 318.90 | -14.46 | 168.80 | -22.47 | -24.00 |
| PFOA | 413.00 | 369.00 | -15.31 | 169.00 | -22.94 | -40.75 |
| PFNA | 462.70 | 419.10 | -15.50 | 218.80 | -23.72 | -40.18 |
| PFDoA | 612.80 | 569.00 | -18.68 | 219.10 | -27.84 | -34.40 |
| PFBS | 298.70 | 80.10 | -65.78 | 99.00 | -50.19 | -50.87 |
| PFHxS | 398.90 | 79.80 | -81.04 | 98.90 | -76.72 | -81.72 |
| PFOS | 498.70 | 79.60 | -98.19 | 98.90 | -92.08 | -67.40 |

Analysis results of PFASs degradation products by UPLC-QTOF

Table S2 Qualitative analysis of biomimetic degradation products of PFOS

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Non-isotopic quasi-molecular ions | | | | Isotopic quasi-molecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| L-PFOS | $C_8F_{17}O_3S^-$ | 4.452 | 498.9330 | 4346969.50 | 498.9302 | 5.6120 | 499.9352 | 408758.12 | 499.9333 | 3.8005 |
| Br-PFOS | | 4.320 | 498.9317 | 1069167.88 | 498.9302 | 3.0064 | 499.9349 | 94215.08 | 499.9333 | 3.2004 |
| Perfluoroalkane sulfonic acids | | | | | | | | | | |
| PFBS | $C_4F_9O_3S^-$ | 3.3610 | 298.9446 | 298714.91 | 298.943 | 5.3522 | 299.9472 | 12479.91 | 299.9458 | 4.6675 |
| PFHxS | $C_6F_{13}O_3S^-$ | 3.7750 | 398.9379 | 28549.75 | 398.9366 | 3.2587 | 399.9410 | 1851.61 | 399.9395 | 3.7506 |
| PFHpS | $C_7F_{15}O_3S^-$ | 4.0800 | 448.9354 | 283329.31 | 448.9334 | 4.4550 | 449.9381 | 21454.69 | 449.9364 | 3.7783 |
| Perfluorocarboxylic acids | | | | | | | | | | |
| PFBA | $C_4F_7O_2^-$ | 3.1470 | 212.9805 | 618.00 | 212.9792 | 6.1038 | 213.9862 | 266.00 | 213.9826 | 16.8235 |
| PFPeA | $C_5F_9O_2^-$ | 3.3370 | 262.9759 | 1410.00 | 262.9760 | -0.3803 | 263.9800 | 246.00 | 263.9794 | 2.2729 |
| PFHpA | $C_7F_{13}O_2^-$ | 3.7750 | 362.9703 | 2413.45 | 362.9696 | 1.9285 | 363.9718 | 495.00 | 363.9730 | -3.2970 |
| PFOA | $C_8F_{15}O_2^-$ | 4.0720 | 412.9671 | 573.00 | 412.9664 | 1.6951 | 413.9718 | 343.20 | 413.9698 | 4.8312 |
| PFDA | $C_{10}F_{19}O_2^-$ | 5.0560 | 512.9617 | 8743.58 | 512.9600 | 3.3141 | 513.9652 | 950.00 | 513.9634 | 3.5022 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 6.4940 | 612.9601 | 420.00 | 612.9537 | 10.4411 | 613.9533 | 217.83 | 613.9570 | -6.0265 |

Table S2 Qualitative analysis of biomimetic degradation products of PFOS (continued)

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Non-isotopic quasi-molecular ions | | | | Isotopic quasi-molecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| Polyfluorinated acids | | | | | | | | | | |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 3.3860 | 344.9798 | 1575.50 | 344.9790 | 2.3190 | 345.9808 | 216.00 | 345.9824 | -4.6245 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 3.5510 | 394.9772 | 2023.32 | 394.9758 | 3.5445 | 395.9757 | 235.00 | 395.9792 | -8.8389 |
| H-PFNA | $C_9HF_{16}O_2^-$ | 3.7420 | 444.9734 | 2192.22 | 444.9727 | 1.5731 | 445.9774 | 325.10 | 445.9760 | 3.1392 |
| H-PFHxS | $C_6HF_{12}O_3S^-$ | 3.3940 | 380.9466 | 1620.00 | 380.9460 | 1.5750 | 381.9479 | 492.00 | 381.9494 | -3.9272 |
| H-PFOS | $C_8HF_{16}O_3S^-$ | 4.2790 | 480.9408 | 1485.00 | 480.9397 | 2.2872 | 481.9416 | 222.00 | 481.9427 | -2.2824 |
| H-perfluoroalkanes | | | | | | | | | | |
| Heptafluoropropane | $C_3F_7^-$ | 3.1710 | 168.9902 | 3150.71 | 168.9894 | 4.7340 | 169.9942 | 244.00 | 169.9927 | 8.8238 |
| Nonafluorobutane | $C_4F_9^-$ | 3.3360 | 218.9869 | 4036.28 | 218.9862 | 3.1965 | 219.9893 | 327.00 | 219.9895 | -0.9091 |
| Undecafluoropentane | $C_5F_{11}^-$ | 3.5270 | 268.9847 | 2026.60 | 268.9836 | 4.0895 | 269.9873 | 398.00 | 269.9863 | 3.7039 |
| H-perfluorohexane | $C_6F_{13}^-$ | 3.7910 | 318.9805 | 3348.27 | 318.9798 | 2.1945 | 319.9860 | 216.00 | 319.9831 | 9.0629 |
| Undecafluoroheptane | $C_7F_{15}^-$ | 4.0720 | 368.9785 | 715.00 | 368.9768 | 4.6073 | 369.9792 | 279.00 | 369.9800 | -2.1623 |
| H-Perfluorononane | $C_9F_{21}^-$ | 5.1140 | 468.9723 | 5547.96 | 468.9702 | 4.4779 | 469.9763 | 649.00 | 469.9736 | 5.7450 |

Table S3 Peak areas of PFOS and its potential degradation products in decomposition sample and various controls

| Degradation products | Molecular formula [M-H]- | Theoretical m/z (Da) | PFOS+$VB_{12}$+$nFe^0$/$Ni^0$ | | PFOS+$nFe^0$/$Ni^0$ | | PFOS+$VB_{12}$ | | PFOS-adsorption | | PFOS-blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| L-PFOS | $C_8F_{17}O_3S^-$ | 498.9302 | 4.452 | 27919000.02 | 4.453 | 29360888.73 | 4.462 | 31886457.48 | 4.456 | 31715805.16 | 4.493 | 32755342.53 |
| Br-PFOS | | 498.9302 | 4.320 | 6092418.54 | 4.321 | 8752665.51 | 4.321 | 9612328.80 | 4.323 | 9462636.07 | 4.319 | 9866088.67 |
| Perfluoroalkane sulfonic acids | | | | | | | | | | | | |
| PFBS | $C_4F_9O_3S^-$ | 298.943 | 3.361 | 1334010.39 | 3.378 | 1444946.98 | 3.371 | 1297223.78 | 3.373 | 1343781.99 | 3.373 | 1368766.86 |
| PFHxS | $C_6F_{13}O_3S^-$ | 398.9366 | 3.775 | 125839.39 | 3.742 | 128212.59 | 3.767 | 127882.33 | 3.770 | 124489.13 | 3.773 | 130885.07 |
| PFHpS | $C_7F_{15}O_3S^-$ | 448.9334 | 4.080 | 1504661.40 | 4.073 | 1713425.54 | 4.073 | 1696906.56 | 4.075 | 1717337.94 | 4.071 | 1757637.13 |
| Perfluorocarboxylic acids | | | | | | | | | | | | |
| PFBA | $C_4F_7O_2^-$ | 212.9792 | 3.147 | 5026.83 | 3.147 | 3185.64 | - | - | 3.199 | 3192.76 | - | - |
| PFPeA | $C_5F_9O_2^-$ | 262.9760 | 3.337 | 9853.25 | 3.321 | 9663.53 | - | - | 3.307 | 9315.02 | 3.410 | 9107.00 |
| PFHpA | $C_7F_{13}O_{2-}$ | 362.9696 | 3.775 | 7860.66 | 3.078 | 7854.90 | 3.80 | 8001.40 | 3.753 | 8845.83 | 3.798 | 8537.40 |
| PFOA | $C_8F_{15}O_{2-}$ | 412.9664 | 4.072 | 2333.33 | 4.114 | 3473.27 | - | - | - | - | - | - |
| PFDA | $C_{10}F_{19}O_2^-$ | 512.9600 | 5.056 | 42871.54 | 5.106 | 14216.87 | 5.098 | 11415.56 | 5.092 | 10979.58 | 5.104 | 11809.00 |
| PFDoA | $C_{12}F_{23}O_2$- | 612.9537 | 6.494 | 4271.17 | - | - | 6.536 | 1000.54 | - | - | 6.534 | 1114.60 |

Table S3 Peak areas of PFOS and its potential degradation products in decomposition sample and various controls (continued)

| Degradation products | Molecular formula [M-H]- | Theoretical m/z (Da) | PFOS+$VB_{12}$+$nFe^0$/$Ni^0$ | | PFOS+$nFe^0$/$Ni^0$ | | PFOS+$VB_{12}$ | | PFOS-adsorption | | PFOS-blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| Polyfluorinated acids | | | | | | | | | | | | |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 344.9790 | 3.386 | 8310.59 | 3.411 | 9128.99 | 3.412 | 7701.25 | 3.389 | 7385.64 | 3.435 | 9229.78 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 394.9758 | 3.551 | 6408.27 | - | - | - | - | - | - | 3.534 | 7746.74 |
| H-PFNA | $C_9HF_{16}O_2^-$ | 444.9727 | 3.742 | 8011.38 | 3.767 | 8930.77 | 3.751 | 7375.52 | 3.761 | 7802.32 | 3.740 | 8760.03 |
| H-PFHxS | $C_6HF_{12}O_3S^-$ | 380.9460 | 3.394 | 6396.01 | 3.4280 | 5623.05 | 3.395 | 5132.93 | 3.414 | 5546.89 | 3.393 | 5312.49 |
| H-PFOS | $C_8HF_{16}O_3S^-$ | 480.9397 | 4.279 | 7341.25 | 4.2960 | 8049.77 | - | - | 4.274 | 4076.78 | 4.269 | 8475.55 |
| H-perfluoroalkanes | | | | | | | | | | | | |
| Heptafluoropropane | $C_3F_7^-$ | 168.9894 | 3.171 | 13447.55 | - | - | 3.197 | 7776.35 | 3.150 | 9448.46 | 3.178 | 19470.29 |
| Nonafluorobutane | $C_4F_9^-$ | 218.9862 | 3.336 | 21549.59 | 3.3620 | 17760.20 | 3.354 | 17904.63 | 3.348 | 21233.22 | 3.360 | 19381.38 |
| Undecafluoropentane | $C_5F_{11}^-$ | 268.9836 | 3.527 | 7984.31 | - | - | - | - | 3.571 | 5743.15 | 3.550 | 6528.33 |
| H-perfluorohexane | $C_6F_{13}^-$ | 318.9798 | 3.791 | 13919.93 | 3.7830 | 12865.27 | 3.792 | 12307.66 | 3.786 | 13168.24 | 3.757 | 13071.70 |
| Undecafluoroheptane | $C_7F_{15-}$ | 368.9768 | 4.072 | 2935.35 | - | - | - | - | 4.984 | 3469.31 | 4.079 | 2483.27 |
| H-Perfluorononane | $C_9F_{21}^-$ | 468.9702 | 5.114 | 27858.73 | 5.1230 | 8589.79 | 5.073 | 7908.60 | 5.117 | 7527.44 | 5.096 | 9072.00 |

Table S4 Qualitative analysis of biomimetic degradation products of PFHxS

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Non-isotopic quasi-molecular ions | | | | Isotopic quasi-molecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| PFHxS | $C_6F_{13}O_3S^-$ | 3.7740 | 398.9389 | 5373773.00 | 398.9366 | 5.7653 | 399.9406 | 401533.62 | 399.9395 | 2.7504 |
| Perfluoroalkane sulfonic acids | | | | | | | | | | |
| PFBS | $C_4F_9O_3S^-$ | 3.3780 | 298.9438 | 373987.28 | 298.943 | 2.6761 | 299.9466 | 18550.54 | 299.9458 | 2.6671 |
| PFPeS | $C_5F_{11}O_3S^-$ | 3.5620 | 348.9406 | 100749.26 | 348.9398 | 2.2927 | 349.9425 | 5816.54 | 349.9427 | -0.5715 |
| PFHpS | $C_7F_{15}O_3S^-$ | 4.0800 | 448.9342 | 915.52 | 448.9334 | 1.7820 | 449.9233 | 213.97 | 449.9364 | -29.1161 |
| L-PFOS | $C_8F_{17}O_3S^-$ | 4.469 | 498.9308 | 8679.89 | 498.9302 | 1.2026 | 499.9336 | 716.15 | 499.9333 | 0.6001 |
| Br-PFOS | | 4.345 | 498.9259 | 1666.22 | 498.9302 | -8.6185 | 499.9340 | 227.00 | 499.9333 | 1.4002 |
| Perfluorocarboxylic acids | | | | | | | | | | |
| PFPeA | $C_5F_9O_2^-$ | 3.3470 | 262.9772 | 2616.38 | 262.9760 | 4.5631 | 263.9813 | 265.05 | 263.9794 | 7.1975 |
| PFHxA | $C_6F_{11}O_2^-$ | 3.546 | 312.9721 | 1112.50 | 312.9728 | -2.2366 | 313.9834 | 273.10 | 313.9762 | 22.9311 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| PFDA | $C_{10}F_{19}O_2^-$ | 5.0670 | 512.9599 | 3113.82 | 512.9600 | -0.1949 | 513.9592 | 265.52 | 513.9634 | -8.1719 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 6.4390 | 612.9584 | 688.30 | 612.9537 | 7.6677 | 613.9544 | 319.52 | 613.9570 | -4.2348 |
| PFUdA | $C_{11}F_{21}O_2^-$ | 7.9760 | 712.9461 | 805.00 | 712.9473 | -1.6832 | 713.9482 | 335.90 | 713.9506 | -3.3616 |

Table S4 Qualitative analysis of biomimetic degradation products of PFHxS (continued)

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Non-isotopic quasi-molecular ions | | | | Isotopic quasi-molecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| Polyfluorinated acids | | | | | | | | | | |
| H-PFHxA | $C_6HF_{10}O_2^-$ | 3.3610 | 294.9831 | 606.00 | 294.9822 | 3.0510 | 295.9849 | 240.43 | 295.9856 | -2.3650 |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 3.419 | 344.9803 | 2842.87 | 344.9790 | 3.7683 | 345.9790 | 220.60 | 345.9824 | -9.8272 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 3.5510 | 394.9772 | 2149.71 | 394.9758 | 3.5445 | 395.9781 | 403.90 | 395.9792 | -2.7779 |
| H-PFHxS | $C_6HF_{12}O_3S^-$ | 3.3860 | 380.9449 | 1215.00 | 380.9460 | -2.8876 | 381.9469 | 232.00 | 381.9494 | -6.5454 |
| H-PFOS | $C_8HF_{16}O_3S^-$ | 3.7740 | 480.9401 | 53946.24 | 480.9397 | 0.8317 | 481.9421 | 5790.00 | 481.9427 | -1.2450 |
| H-perfluoroalkanes | | | | | | | | | | |
| Nonafluorobutane | $C_4F_9^-$ | 3.3360 | 218.9867 | 3926.81 | 218.9862 | 2.2832 | 219.9907 | 234.70 | 219.9895 | 5.4548 |
| Undecafluoropentane | $C_5F_{11}^-$ | 3.5680 | 268.9836 | 1846.70 | 268.9836 | 0.0000 | 269.9875 | 270.00 | 269.9863 | 4.4447 |
| H-perfluorohexane | $C_6F_{13}^-$ | 3.7990 | 318.9798 | 1650.00 | 318.9798 | 0.0000 | 319.9867 | 287.00 | 319.9831 | 11.2505 |
| H-Perfluorononane | $C_9F_{21}^-$ | 5.0960 | 468.9731 | 1731.95 | 468.9702 | 6.1837 | 469.9725 | 296.00 | 469.9736 | -2.3406 |

Table S5 Peak areas of PFHxS and its potential degradation products in decomposition sample and various controls

| Degradation products | Molecular formula [M-H]- | Theoretical m/z (Da) | PFHxS+$VB_{12}$+$nFe^0$/$Ni^0$ | | PFHxS+$nFe^0$/$Ni^0$ | | PFHxS+$VB_{12}$ | | PFHxS-adsorption | | PFHxS-blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| PFHxS | $C_6F_{13}O_3S^-$ | 398.9366 | 3.774 | 27824828.47 | 3.767 | 33109353.82 | 3.772 | 32602270.46 | 3.769 | 32990106.12 | 3.770 | 33315195.38 |
| Perfluoroalkane sulfonic acids | | | | | | | | | | | | |
| PFBS | $C_4F_9O_3S^-$ | 298.943 | 3.378 | 1663376.11 | 3.378 | 1834918.34 | 3.375 | 1724203.15 | 3.373 | 1794092.89 | 3.373 | 1656230.20 |
| PFPeS | $C_5F_{11}O_3S^-$ | 348.9398 | 3.562 | 412299.43 | 3.560 | 457025.23 | 3.557 | 437467.58 | 3.563 | 443068.78 | 3.563 | 442942.36 |
| PFHpS | $C_7F_{15}O_3S^-$ | 448.9334 | 4.080 | 5048.78 | 4.064 | 2767.06 | 4.070 | 4341.90 | 4.084 | 3593.82 | 4.068 | 1731.18 |
| L-PFOS | $C_8F_{17}O_3S^-$ | 498.9302 | 4.469 | 44762.99 | 4.469 | 25610.06 | 4.475 | 24539.72 | 4.472 | 27875.10 | 4.489 | 34592.45 |
| Br-PFOS | | 498.9302 | 4.345 | 11250.82 | 4.370 | 8254.28 | 4.342 | 6558.91 | 4.315 | 7593.34 | 4.315 | 8338.20 |
| Perfluorocarboxylic acids | | | | | | | | | | | | |
| PFPeA | $C_5F_9O_2^-$ | 262.9760 | 3.347 | 11515.18 | 3.304 | 10856.05 | 3.318 | 11274.91 | 3.373 | 9291.55 | 3.373 | 9981.72 |
| PFHxA | $C_6F_{11}O_2^-$ | 312.9728 | 3.546 | 5256.96 | - | - | - | - | - | - | 3.572 | 5127.55 |
| PFDA | $C_{10}F_{19}O_2^-$ | 512.9600 | 5.067 | 15654.23 | 5.106 | 46258.62 | 5.095 | 13894.65 | 5.051 | 16033.26 | 5.076 | 14493.33 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 612.9537 | 6.439 | 5891.05 | 6.536 | 4182.77 | - | - | 6.505 | 4143.11 | - | - |
| PFUdA | $C_{11}F_{21}O_2^-$ | 712.9473 | 7.976 | 4660.880 | - | - | 7.996 | 8454.12 | - | - | - | - |

Table S5 Peak areas of PFHxS and its potential degradation products in decomposition sample and various controls (continued)

| Degradation products | Molecular formula [M-H]- | Theoretical m/z (Da) | PFHxS+$VB_{12}$+$nFe^0/Ni^0$ | | PFHxS+$nFe^0/Ni^0$ | | PFHxS+$VB_{12}$ | | PFHxS-adsorption | | PFHxS-blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| Polyfluorinated acids | | | | | | | | | | | | |
| H-PFHxA | $C_6F_{13}O_3S^-$ | 294.9822 | 3.361 | 8284.27 | 3.304 | 9800.36 | 3.293 | 10626.64 | 3.290 | 10098.12 | 3.282 | 8581.98 |
| H-PFHpA | $C_6HF_{10}O_2^-$ | 344.9790 | 3.419 | 10981.52 | 3.403 | 10800.83 | 3.417 | 12693.58 | 3.431 | 11667.65 | 3.400 | 11225.87 |
| H-PFOA | $C_7HF_{12}O_2^-$ | 394.9758 | 3.551 | 8876.11 | 3.527 | 8453.16 | 3.557 | 9661.91 | 3.538 | 10951.11 | 3.563 | 11266.94 |
| H-PFHxS | $C_8HF_{14}O_2^-$ | 380.9460 | 3.386 | 257357.61 | 3.676 | 9968.24 | 3.359 | 10333.32 | 3.389 | 11237.70 | 3.406 | 14099.02 |
| H-PFOS | $C_6HF_{12}O_3S^-$ | 480.9397 | 3.774 | 257357.61 | 3.758 | 302133.94 | 3.7390 | 294913.49 | 3.761 | 295561.43 | 3.770 | 294776.00 |
| H-perfluoroalkanes | | | | | | | | | | | | |
| Nonafluorobutane | $C_4F_9^-$ | 218.9862 | 3.336 | 23887.53 | 3.370 | 25088.24 | 3.395 | 22757.00 | 3.348 | 23977.35 | 3.357 | 24679.09 |
| Undecafluoropentane | $C_5F_{11}^-$ | 268.9836 | 3.568 | 9629.00 | 3.552 | 10522.95 | 3.574 | 11195.42 | 3.546 | 11163.52 | 3.563 | 10798.02 |
| H-perfluorohexane | $C_6F_{13}^-$ | 318.9798 | 3.799 | 6178.70 | 3.808 | 6781.68 | - | - | 3.877 | 6757.29 | 3.820 | 6995.13 |
| H-Perfluorononane | $C_9F_{21}^-$ | 468.9702 | 5.096 | 8113.06 | 5.073 | 29649.90 | 5.103 | 9237.120 | 5.092 | 10941.53 | 5.101 | 9403.14 |

Table S6 Qualitative analysis of biomimetic degradation products of PFBS

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Non-isotopic quasi-molecular ions | | | | Isotopic quasi-molecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| PFBS | $C_4F_9O_3S^-$ | 3.405 | 298.9444 | 573190.00 | 298.943 | 4.6831 | 299.9468 | 218086.67 | 299.9458 | 3.3339 |
| Perfluoroalkane sulfonic acids | | | | | | | | | | |
| PFHxS | $C_6F_{13}O_3S^-$ | 3.777 | 398.9369 | 11125.43 | 398.9366 | 0.7520 | 399.9381 | 747.41 | 399.9395 | -3.5005 |
| PFOS | $C_8F_{17}O_3S^-$ | 4.455 | 498.9311 | 4612.64 | 498.9302 | 1.8039 | 499.9362 | 365.15 | 499.9333 | 5.8007 |
| Perfluorocarboxylic acids | | | | | | | | | | |
| PFPeA | $C_5F_9O_2^-$ | 3.323 | 262.9776 | 1336.05 | 262.9760 | 6.0842 | 263.9828 | 240.03 | 263.9794 | 12.8796 |
| PFHpA | $C_7F_{13}O_2^-$ | 3.777 | 362.9695 | 3106.93 | 362.9696 | -0.2755 | 363.9648 | 438.47 | 363.9730 | -22.5297 |
| PFOA | $C_8F_{15}O_2^-$ | 4.050 | 412.9560 | 639.58 | 412.9664 | -25.1843 | 413.9680 | 272.07 | 413.9698 | -4.3482 |
| PFNA | $C_9F_{17}O_2^-$ | 4.521 | 462.9567 | 244.46 | 462.9632 | -14.0402 | 463.9625 | 243.87 | 463.9666 | -8.8369 |
| PFDA | $C_{10}F_{19}O_2^-$ | 5.067 | 512.9597 | 6219.94 | 512.9600 | -0.5848 | 513.9644 | 1182.35 | 513.9634 | 1.9457 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 6.455 | 612.9535 | 703.94 | 612.9537 | -0.3263 | 613.9592 | 237.03 | 613.9570 | 3.5833 |
| Polyfluorinated acids | | | | | | | | | | |
| H-PFHxA | $C_6HF_{10}O_2^-$ | 3.281 | 294.9827 | 1246.60 | 294.9822 | 1.6950 | 295.9852 | 320.88 | 295.9856 | -1.3514 |

Table S6 Qualitative analysis of biomimetic degradation products of PFBS (continued)

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Non-isotopic quasi-molecular ions | | | | Isotopic quasi-molecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 3.447 | 344.9773 | 1012.14 | 344.9790 | -4.9279 | 345.9844 | 295.25 | 345.9824 | 5.7806 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 3.554 | 394.9744 | 3566.60 | 394.9758 | -3.5445 | 395.9822 | 474.00 | 395.9792 | 7.5761 |
| H-PFNA | $C_9HF_{16}O_2^-$ | 3.744 | 444.9730 | 2207.98 | 444.9727 | 0.6742 | 445.9777 | 565.10 | 445.9760 | 3.8118 |
| | | | | | H-perfluoroalkanes | | | | | |
| Heptafluoropropane | $C_3F_7^-$ | 3.157 | 168.9902 | 3481.92 | 168.9894 | 4.7340 | 169.9913 | 208.21 | 169.9927 | -8.2357 |
| Nonafluorobutane | $C_4F_9^-$ | 3.331 | 218.9878 | 3549.39 | 218.9862 | 7.3063 | 219.9919 | 313.92 | 219.9895 | 10.9095 |
| Undecafluoropentane | $C_5F_{11}^-$ | 3.562 | 268.9837 | 2780.58 | 268.9836 | 0.3718 | 269.9847 | 241.00 | 269.9863 | -5.9263 |
| H-perfluorohexane | $C_6F_{13}^-$ | 3.786 | 318.9793 | 5575.27 | 318.9798 | -1.5675 | 319.9861 | 414.69 | 319.9831 | 9.3754 |
| H-Perfluorononane | $C_9F_{21}^-$ | 5.059 | 468.9705 | 4675.56 | 468.9702 | 0.6397 | 469.9745 | 393.05 | 469.9736 | 1.9150 |

Table S7 Peak areas of PFBS and its potential degradation products in decomposition sample and various controls

| Degradation products | Molecular formula $[M-H]^-$ | Theoretical m/z (Da) | PFBS+$VB_{12}$+$nFe^0/Ni^0$ | | PFBS+$nFe^0/Ni^0$ | | PFBS+$VB_{12}$ | | PFBS- adsorption | | PFBS- blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| PFBS | $C_4F_9O_3S^-$ | 298.9438 | 3.405 | 23417054.07 | 3.404 | 22045146.01 | 3.405 | 23583908.19 | 3.405 | 25252896.90 | 3.399 | 26302059.48 |
| Perfluoroalkane sulfonic acids | | | | | | | | | | | | |
| PFHxS | $C_6F_{13}O_3^-$ | 398.9366 | 3.777 | 12780.06 | 3.784 | 14387.64 | 3.777 | 15251.72 | 3.786 | 16261.51 | 3.796 | 12543.23 |
| PFOS | $C_8F_{17}O_3S^-$ | 498.9302 | 4.455 | 19210.60 | 4.454 | 17842.39 | 4.479 | 20536.61 | 4.480 | 24795.62 | 4.457 | 20910.59 |
| Perfluorocarboxylic acids | | | | | | | | | | | | |
| PFPeA | $C_5F_9O_2^-$ | 262.9760 | 3.323 | 7595.44 | 3.346 | 7765.39 | 3.314 | 6324.69 | 3.347 | 6128.88 | 3.325 | 6670.73 |
| PFHpA | $C_7F_{13}O_2^-$ | 362.9696 | 3.777 | 12780.06 | 3.784 | 14387.64 | 3.777 | 15251.72 | 3.786 | 16261.51 | 3.796 | 12543.23 |
| PFOA | $C_8F_{15}O_2^-$ | 412.9664 | 4.050 | 3133.14 | 4.074 | 3316.86 | 4.074 | 3659.55 | 4.127 | 4315.38 | 4.077 | 3921.69 |
| PFNA | $C_9F_{17}O_2^-$ | 462.9632 | 4.521 | 1572.79 | - | - | - | - | - | - | - | - |
| PFDA | $C_{10}F_{19}O_2^-$ | 512.9600 | 5.067 | 38962.93 | 5.066 | 19920.16 | 5.058 | 23523.97 | 5.116 | 39073.45 | 5.052 | 36285.92 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 612.9537 | 6.455 | 4159.69 | 6.463 | 3885.58 | 6.447 | 3794.31 | 6.472 | 8390.64 | 6.449 | 6170.86 |
| Polyfluorinated acids | | | | | | | | | | | | |
| H-PFHxA | $C_6HF_{10}O_2^-$ | 294.9822 | 3.281 | 8788.28 | 3.297 | 8521.02 | 3.306 | 9652.59 | 3.290 | 10459.54 | 3.267 | 9010.53 |

Table S7 Peak areas of PFBS and its potential degradation products in decomposition sample and various controls (continued)

| Degradation products | Molecular formula $[M-H]^-$ | Theoretical m/z (Da) | PFBS+$VB_{12}$+$nFe^0/Ni^0$ | | PFBS+$nFe^0/Ni^0$ | | PFBS+$VB_{12}$ | | PFBS- adsorption | | PFBS- blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 344.9790 | 3.447 | 2305.13 | 3.437 | 7048.78 | 3.438 | 6514.25 | 3.430 | 6057.27 | 3.432 | 3998.07 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 394.9758 | 3.554 | 12869.66 | 3.561 | 13239.96 | 3.562 | 12789.82 | 3.554 | 14422.08 | 3.548 | 13414.90 |
| H-PFNA | $C_9HF_{16}O_2^-$ | 444.9727 | 3.744 | 11964.44 | 3.751 | 11714.29 | 3.752 | 11105.32 | 3.752 | 11612.06 | 3.755 | 11108.87 |
| H-perfluoroalkanes | | | | | | | | | | | | |
| Heptafluoropropane | $C_3F_7^-$ | 168.9894 | 3.157 | 11826.66 | 3.173 | 8491.25 | 3.182 | 12910.40 | 3.166 | 14590.56 | 3.151 | 11004.96 |
| Nonafluorobutane | $C_4F_9^-$ | 218.9862 | 3.331 | 17014.51 | 3.338 | 15840.75 | 3.339 | 17747.18 | 3.339 | 18294.60 | 3.317 | 15152.90 |
| Undecafluoropentane | $C_5F_{11}^-$ | 268.9836 | 3.562 | 10505.11 | 3.570 | 10283.51 | 3.545 | 13129.48 | 3.538 | 12266.73 | 3.556 | 11179.73 |
| H-perfluorohexane | $C_6F_{13}^-$ | 318.9798 | 3.786 | 21441.45 | 3.760 | 20816.56 | 3.793 | 22724.12 | 3.786 | 24004.85 | 3.779 | 22332.66 |
| H-Perfluorononane | $C_9F_{21}^-$ | 468.9702 | 5.059 | 24118.06 | 5.074 | 13294.05 | 5.074 | 16728.64 | 5.092 | 24869.80 | 5.052 | 22227.44 |

Table S8 Qualitative analysis of biomimetic degradation products of 8:2 FTOH

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Nonisotopic quasimolecular ions | | | | Isotopic quasimolecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| 8:2FTOH | $C_{12}H_7F_{17}O_3^-$ | - | - | - | 523.0207 | - | - | - | 524.0241 | - |
| Perfluorocarboxylic acids | | | | | | | | | | |
| PFBA | $C_4F_7O_2^-$ | 3.170 | 212.9798 | 3890.83 | 212.9792 | 2.8172 | 213.9798 | 320.00 | 213.9826 | -13.0853 |
| PFPeA | $C_5F_9O_2^-$ | 3.360 | 262.9763 | 2600.00 | 262.9760 | 1.1408 | 263.9801 | 240.00 | 263.9794 | 2.6517 |
| PFHxA | $C_6F_{11}O_2^-$ | 3.559 | 312.9735 | 7786.38 | 312.9728 | 2.2366 | 313.9771 | 639.00 | 313.9762 | 2.8665 |
| PFHpA | $C_7F_{13}O_2^-$ | 3.790 | 362.9699 | 7910.84 | 362.9696 | 0.8265 | 363.9693 | 419.00 | 363.9730 | -10.1657 |
| PFOA | $C_8F_{15}O_2^-$ | 4.063 | 412.9670 | 14391.14 | 412.9664 | 1.4529 | 413.9713 | 773.00 | 413.9698 | 3.6234 |
| PFNA | $C_9F_{17}O_2^-$ | 4.501 | 462.9611 | 700.00 | 462.9632 | -4.5360 | 463.9676 | 222.75 | 463.9666 | 2.1553 |
| PFDA | $C_{10}F_{19}O_2^-$ | 5.104 | 512.9606 | 5422.53 | 512.9600 | 1.1697 | 513.9637 | 401.00 | 513.9634 | 0.5837 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 6.477 | 612.9553 | 1228.00 | 612.9537 | 2.6103 | 613.9561 | 343.00 | 613.9570 | -1.4659 |
| PFTeDA | $C_{14}F_{27}O_{2-}$ | 7.997 | 712.9482 | 6215.55 | 712.9473 | 1.2624 | 713.9467 | 803.00 | 713.9506 | -5.4626 |
| Polyfluorinated acids | | | | | | | | | | |
| H-PFHxA | $C_6HF_{10}O_2^-$ | 3.261 | 294.98 | 1462.95 | 294.9822 | -2.0340 | 295.9852 | 297.50 | 295.9856 | -1.3514 |

Table S8 Qualitative analysis of biomimetic degradation products of 8:2 FTOH (continued)

| Degradation products | Molecular formula [M-H]- | Retention time (min) | Nonisotopic quasimolecular ions | | | | Isotopic quasimolecular ions | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) | Measured m/z (Da) | Abundance (cps) | Theoretical m/z(Da) | DE ($\times10^{-6}$) |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 3.385 | 344.9815 | 3385.00 | 344.9790 | 7.2468 | 345.9815 | 320.00 | 345.9824 | -2.6013 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 3.559 | 394.9760 | 4884.73 | 394.9758 | 0.5064 | 395.9815 | 627.00 | 395.9792 | 5.8084 |
| H-PFNA | $C_9HF_{16}O_2^-$ | 3.732 | 444.9743 | 3530.94 | 444.9727 | 3.5957 | 445.9810 | 308.00 | 445.9760 | 11.2112 |
| 7:3Acid | $C_{10}H_4F_{15}O_2^-$ | 4.749 | 440.9983 | 12451.66 | 440.9977 | 1.3605 | 441.9996 | 1178.00 | 442.0011 | -3.3937 |
| | | | | | H-perfluoroalkanes | | | | | |
| Heptafluoropropane | $C_3F_7^-$ | 3.1450 | 168.9897 | 8811.36 | 168.9894 | 1.7753 | 169.9938 | 287.50 | 169.9927 | 6.4708 |
| Nonafluorobutane | $C_4F_9^-$ | 3.369 | 218.9864 | 10633.32 | 218.9862 | 0.9133 | 219.9902 | 559.00 | 219.9895 | 3.1820 |
| Undecafluoropentane | $C_5F_{11}^-$ | 3.567 | 268.9837 | 16962.99 | 268.9836 | 0.3718 | 269.9870 | 893.00 | 269.9863 | 2.5927 |
| H-perfluorohexane | $C_6F_{13}^-$ | 3.765 | 318.9807 | 11078.48 | 318.9798 | 2.8215 | 319.9885 | 263.00 | 319.9831 | 16.8756 |
| Undecafluoroheptane | $C_7F_{15}^-$ | 4.071 | 368.9777 | 18235.15 | 368.9768 | 2.4392 | 369.9801 | 594.50 | 369.9800 | 0.2703 |
| H-Perfluorononane | $C_9F_{21}^-$ | 5.063 | 468.9701 | 3009.34 | 468.9702 | -0.2132 | 469.9703 | 402.55 | 469.9736 | -7.0217 |
| H-perfluoroundecane | $C_{11}F_{23}^-$ | 6.460 | 568.9617 | 455.00 | 568.9638 | -3.6909 | 569.9756 | 322.00 | 569.9672 | 14.7375 |
| H-perfluorotridecane | $C_{13}F_{27}^-$ | 8.014 | 668.9570 | 1311.00 | 668.9587 | -2.5413 | 669.9701 | 207.85 | 669.9608 | 13.8812 |

Table S9 Peak areas of 8:2 FTOH and its potential degradation products in decomposition sample and various controls

| Degradation products | Molecular formula $[M-H]^-$ | Theoretical m/z (Da) | 8:2FTOH+$VB_{12}$+$nFe^0/Ni^0$ | | 8:2FTOH+$nFe^0/Ni^0$ | | 8:2FTOH+$VB_{12}$ | | 8:2FTOH-adsorption | | 8:2FTOH- blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| 8:2FTOH | $C_{12}H_7F_{17}O_3^-$ | 523.0207 | - | - | - | - | - | - | 7.965 | 3982.39 | 7.993 | 115218.44 |
| Perfluorocarboxylic acids | | | | | | | | | | | | |
| PFBA | $C_4F_7O_2^-$ | 212.9792 | 3.170 | 11625.11 | 3.154 | 11591.54 | 3.170 | 11320.21 | 3.179 | 12873.94 | 3.174 | 15507.38 |
| PFPeA | $C_5F_9O_2^-$ | 262.9760 | 3.360 | 17905.10 | 3.394 | 19994.74 | 3.393 | 18303.07 | 3.369 | 17144.03 | 3.389 | 18124.80 |
| PFHxA | $C_6F_{11}O_2^-$ | 312.9728 | 3.559 | 29483.72 | 3.551 | 34643.69 | 3.567 | 13352.97 | 3.551 | 13216.05 | 3.554 | 14449.89 |
| PFHpA | $C_7F_{13}O_2^-$ | 362.9696 | 3.790 | 28183.62 | 3.791 | 32557.32 | 3.790 | 25550.93 | 3.790 | 22211.06 | 3.778 | 24417.03 |
| PFOA | $C_8F_{15}O_2^-$ | 412.9664 | 4.063 | 63709.34 | 4.096 | 82936.09 | 4.087 | 6260.81 | 4.096 | 6798.60 | 4.067 | 6273.13 |
| PFNA | $C_9F_{17}O_2^-$ | 462.9632 | 4.501 | 2456.70 | 4.543 | 16927.68 | 4.517 | 3050.81 | 4.485 | 2336.35 | 4.521 | 6550.76 |
| PFDA | $C_{10}F_{19}O_2^-$ | 512.9600 | 5.104 | 24147.05 | 5.080 | 22939.80 | 5.104 | 22802.55 | 5.080 | 23173.78 | 5.100 | 24574.44 |
| PFDoA | $C_{12}F_{23}O_2^-$ | 612.9537 | 6.477 | 7175.20 | 6.477 | 9296.75 | 6.468 | 8483.89 | 6.477 | 15009.83 | 6.480 | 13815.26 |
| PFTeDA | $C_{14}F_{27}O_{2-}$ | 712.9473 | 7.997 | 40316.34 | 7.981 | 8173.88 | 7.997 | 87308.41 | 7.989 | 8231.88 | 8.034 | 5446.02 |
| Polyfluorinated acids | | | | | | | | | | | | |
| H-PFHxA | $C_6HF_{10}O_2^-$ | 294.9822 | 3.261 | 9711.63 | 3.278 | 11071.85 | 3.302 | 11107.11 | 3.253 | 9393.42 | 3.282 | 11481.00 |

Table S9 Peak areas of 8:2 FTOH and its potential degradation products in decomposition sample and various controls (continued)

| Degradation products | Molecular formula $[M-H]^-$ | Theoretical m/z (Da) | 8:2FTOH+$VB_{12}$+$nFe^0/Ni^0$ | | 8:2FTOH+$nFe^0/Ni^0$ | | 8:2FTOH+$VB_{12}$ | | 8:2FTOH-adsorption | | 8:2FTOH- blank | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas | RT (min) | Peak areas |
| H-PFHpA | $C_7HF_{12}O_2^-$ | 344.9790 | 3.385 | 14341.11 | 3.410 | 15080.73 | 3.409 | 15048.31 | 3.418 | 13820.20 | 3.397 | 12518.77 |
| H-PFOA | $C_8HF_{14}O_2^-$ | 394.9758 | 3.559 | 17957.64 | 3.551 | 16621.42 | 3.542 | 14750.10 | 3.534 | 17101.06 | 3.554 | 16777.71 |
| H-PFNA | $C_9HF_{16}O_2^-$ | 444.9727 | 3.732 | 11908.77 | 3.758 | 14098.96 | 3.748 | 10544.66 | 3.765 | 11680.73 | 3.758 | 12425.81 |
| 7:3Acid | $C_{10}H_4F_{15}O_2^-$ | 440.9977 | 4.749 | 63356.55 | 4.766 | 60680.84 | 4.765 | 58328.31 | 4.766 | 74214.25 | 4.769 | 61806.74 |
| | | | | | H-perfluoroalkanes | | | | | | | |
| Heptafluoropropane | $C_3F_7^-$ | 168.9894 | 3.145 | 29699.50 | 3.154 | 38535.23 | 3.170 | 32895.62 | 3.170 | 31693.32 | 3.158 | 43965.52 |
| Nonafluorobutane | $C_4F_9^-$ | 218.9862 | 3.369 | 41563.88 | 3.353 | 44564.50 | 3.385 | 42089.16 | 3.360 | 41329.62 | 3.364 | 41107.15 |
| Undecafluoropentane | $C_5F_{11}^-$ | 268.9836 | 3.567 | 61489.86 | 3.559 | 74491.62 | 3.542 | 28190.86 | 3.559 | 28610.31 | 3.554 | 28870.56 |
| H-perfluorohexane | $C_6F_{13}^-$ | 318.9798 | 3.765 | 43643.45 | 3.791 | 49872.54 | 3.765 | 40244.78 | 3.782 | 33442.12 | 3.778 | 36329.88 |
| Undecafluoroheptane | $C_7F_{15}^-$ | 368.9768 | 4.071 | 74401.40 | 4.088 | 99545.04 | 4.087 | 6790.89 | 4.080 | 8233.31 | 4.092 | 6861.69 |
| H-Perfluorononane | $C_9F_{21}^-$ | 468.9702 | 5.063 | 15609.02 | 5.105 | 14533.78 | 5.063 | 13657.92 | 5.088 | 14927.83 | 5.108 | 16319.03 |
| H-perfluoroundecane | $C_{11}F_{23}^-$ | 568.9638 | 6.460 | 2123.11 | - | - | 6.493 | 3519.19 | 6.485 | 5115.06 | 6.456 | 5571.08 |
| H-perfluorotridecane | $C_{13}F_{27}^-$ | 668.9587 | 8.014 | 8952.99 | - | - | 7.007 | 20873.51 | - | - | 8.034 | 431.34 |

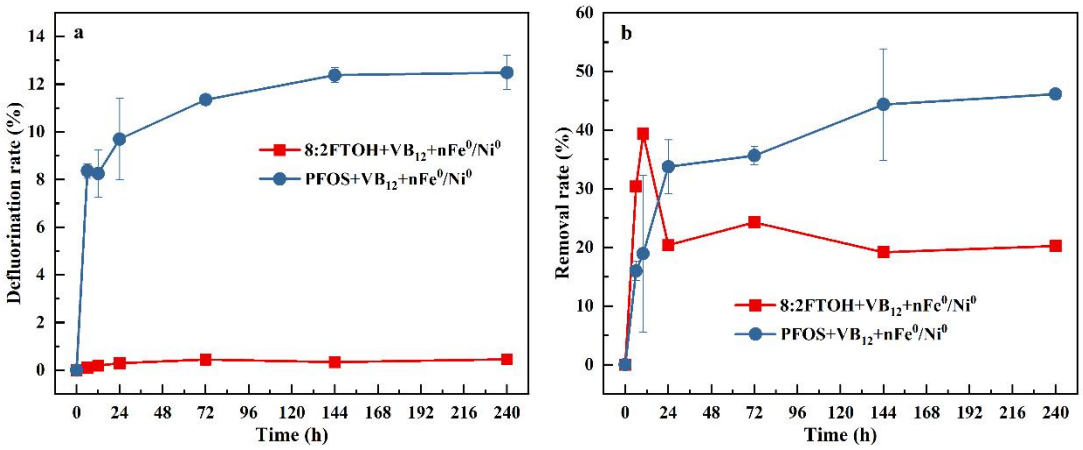


**Figure S1.** Time profiles of defluorination rate (a) removal rate (b) of decomposition treatments for 8:2 FTOH and PFOS. The experiment conditions: $[PFASs]_0$ = 200 μM, $[VB_{12}]_0$ = 200 μM, $[0.5wt\%nFe^0/Ni^0]_0$ = 3.0 g/L, $pH_i$ = 9.5, and T = 60 ºC.

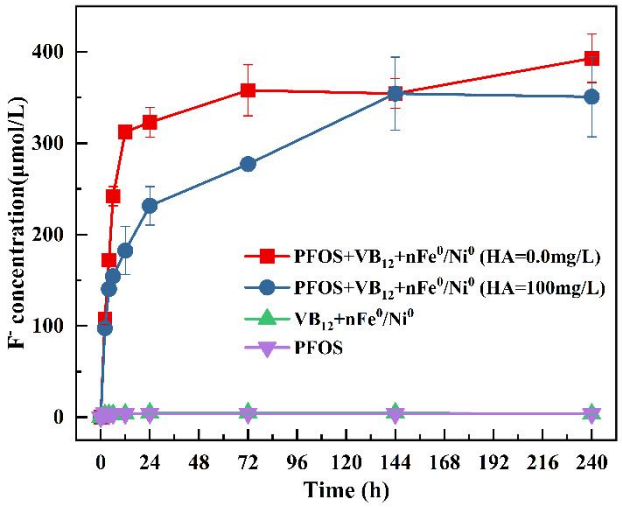


**Figure S2.** Fluoride ion concentration under different HA concentrations. The experiment conditions: $[PFOS]_0$ = 200 μM, $[VB_{12}]_0$ = 200 μM, $[0.5wt\%nFe^0/Ni^0]_0$ = 3.0 g/L, $pH_i$ = 9.5, and T = 60 ºC

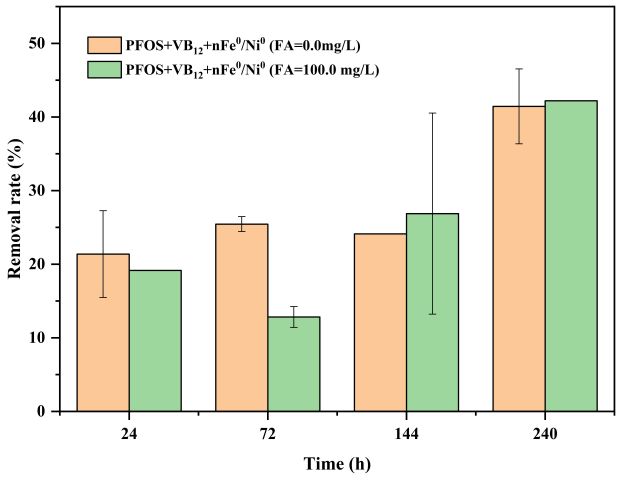


**Figure S3.** Removal rate of PFOS with the FA=100.0 mg/L. The experiment conditions: $[PFOS]_0$ = 200 μM, $[VB_{12}]_0$ = 200 μM, $[0.5wt\%nFe^0/Ni^0]_0$ = 3.0 g/L, $pH_i$ = 9.5, and T = 60 ºC

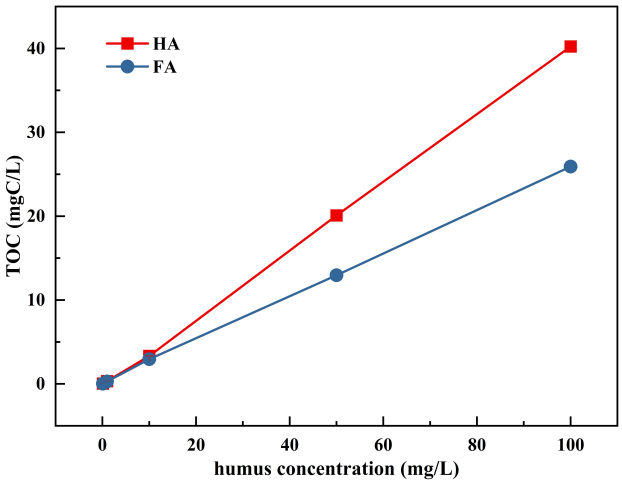


**Figure S4.** Total organic carbon concentration with different humus concentrations.

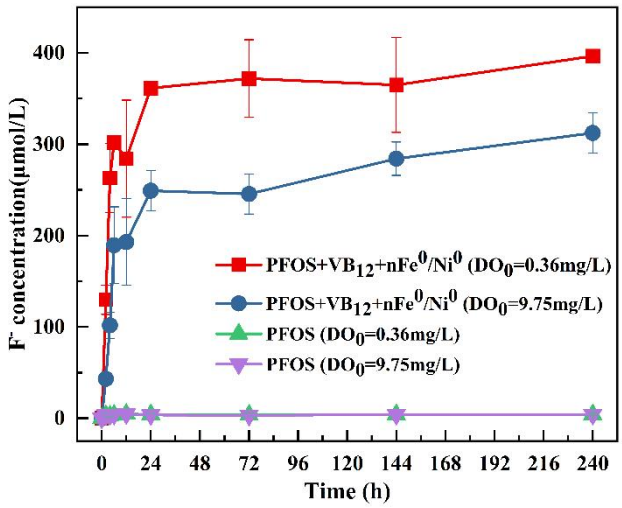


**Figure S5.** Fluoride ion concentration under different initial DO concentrations. The experiment conditions: $[PFOS]_0$ = 200 μM, $[VB_{12}]_0$ = 200 μM, $[0.5wt\%nFe^0/Ni^0]_0$ = 3.0 g/L, $pH_i$ = 9.5, and T = 60 ºC

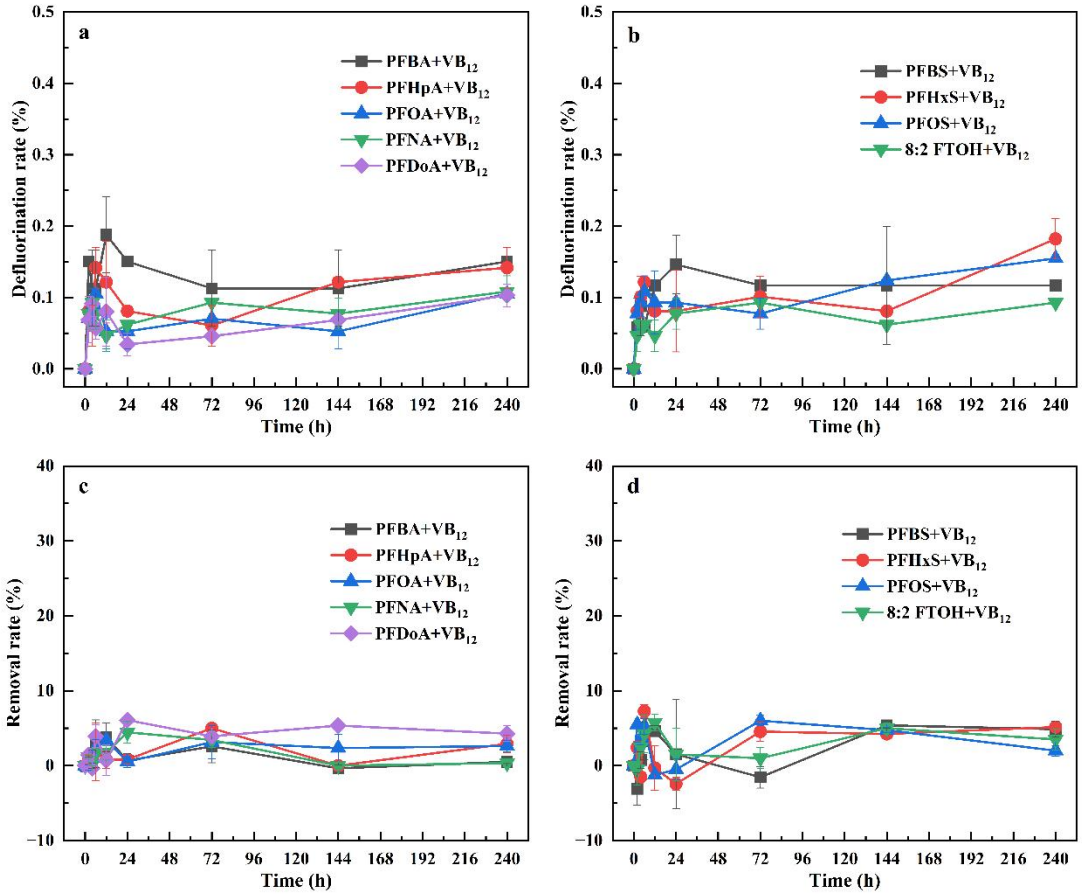


**Figure S6.** Time profiles of defluorination rate of PFCAs (a), PFSAs and 8:2 FTOH (b), removal rate of PFCAs (c), PFSAs and 8:2 FTOH (d) in $VB_{12}$ system. The experiment conditions: $[PFASs]_0$ = 200 μM, $[VB_{12}]_0$ = 200 μM, $pH_i$ = 9.5, and T = 60 ºC.

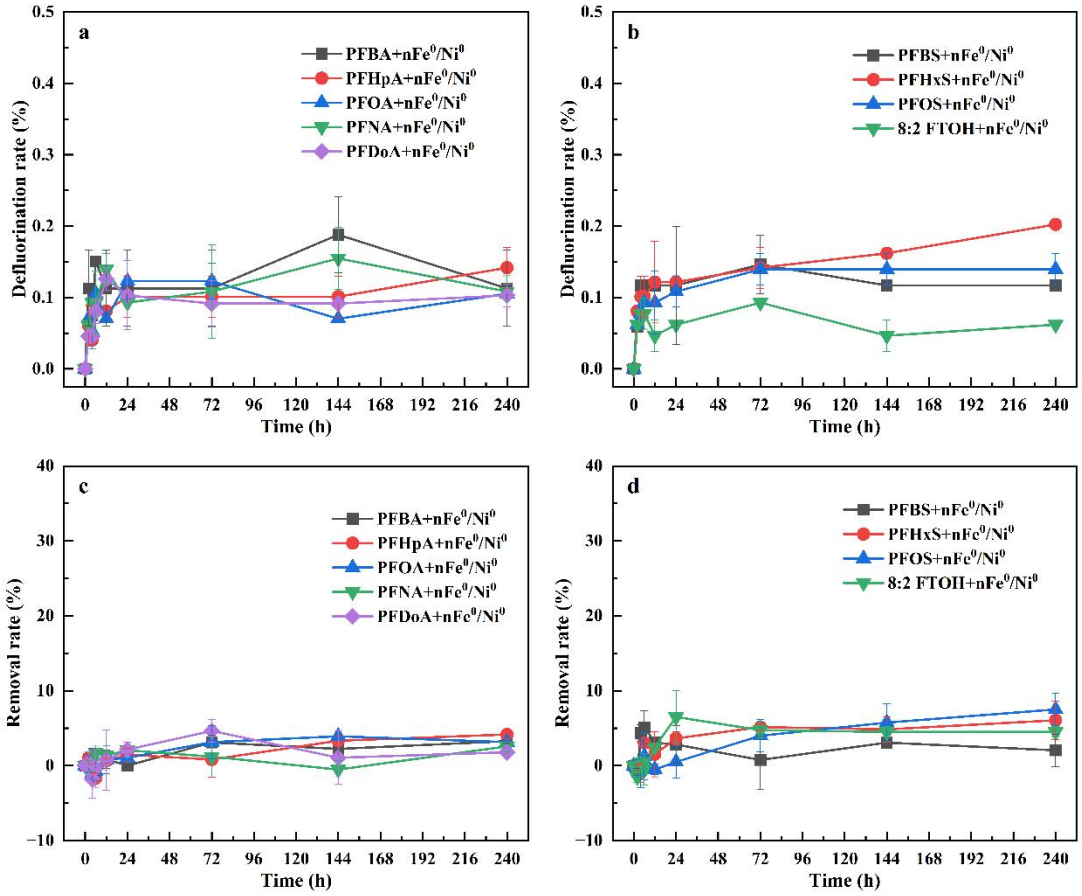


**Figure S7.** Time profiles of defluorination rate of PFCAs (a), PFSAs and 8:2 FTOH (b), removal rate of PFCAs (c), PFSAs and 8:2 FTOH (d) in $nFe^0/Ni^0$ system. The experiment conditions: $[PFASs]_0$ = 200 μM, $[0.5wt\%nFe^0/Ni^0]_0$ = 3.0 g/L, $pH_i$ = 9.5, and T = 60 ºC.