Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Electronic Supplementary Information

Degradation of PFOS by MnO_2/ H_2O_2 Process

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2 texts

4 tables

7 figures

Text S1. Synthesis of different MnO_2 polymorphss

1. α-MnO_2

   0.2 g of $MnSO_4 \cdot H_2O$ (1.18×10^{-3} moles) and 0.5 g of $KMnO_4$ (3.16×10^{-3} moles) were dissolved in 80 ml DI water with vigorously stirring for 30 min. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and dried at 140 °C for 12 h. After cooling down to room temperature, the supernatant was discarded and the remaining solid was filtered, washed by DI water and dried in oven at 80 °C for 12 h. The obtained powder was grinded and stored before use.

2. β-MnO_2

   1.268 g of $MnSO_4 \cdot H_2O$ (0.075 moles) and 0.79 g of $KMnO_4$ (0.05 moles) were dissolved in 80 ml 0.2 M HNO_3 with vigorously stirring for 30 min. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and dried at 180 °C for 12 h. After cooling down to room temperature, the supernatant was discarded and the remaining solid was filtered, washed by DI water and dried in oven at 80 °C for 12h. The obtained powder was grinded and stored before use.

3. γ-MnO_2

   3.375 g of $MnSO_4 \cdot H_2O$ (0.02 moles) and 4.575 g of $(NH_4)_2S_2O_8$ (0.02 moles) were dissolved in 80 ml deionized water with vigorously stirring for 30 min. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and dried at 90 °C for 24 h. After cooling down to room temperature, the supernatant was discarded and the remaining solid was filtered, washed by DI water and dried in oven at 80 °C for 12h. The solid was then calcined at 300 °C for 2 h. The obtained powder was grinded and stored before use.

Text S2. Degradation pathways of PFOS

1. Chain-shortening

$$C_8F_{17}SO_3^{\,-} \rightarrow C_8F_{17}^{\bullet} + SO_3^{\bullet\,-} \tag{1}$$

$$C_8F_{17}^{\bullet} + OH^{\bullet} \rightarrow C_8F_{17}OH \tag{2}$$

$$C_8F_{17}OH \rightarrow C_7F_{15}COF + F^{-} + H^{+} \tag{3}$$

$$C_7F_{15}COF + H_2O \rightarrow C_7F_{15}COO^{-} + F^{-} + 2H^{+} \tag{4}$$

$$C_7F_{15}COO^{-} \rightarrow C_7F_{15}^{\bullet} + COO^{\bullet\,-} \tag{5}$$

$$C_7F_{15}^{\bullet} + OH^{\bullet} \rightarrow C_7F_{15}OH \tag{6}$$

$$C_7F_{15}OH \rightarrow C_6F_{13}COF + F^{-} + H^{+} \tag{7}$$

$$C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COO^{-} + F^{-} + 2H^{+} \tag{8}$$

2. Direct H/F exchange

$$C_7F_{15}COO^{-} \xrightarrow{O_2^{\bullet\,-}} C_7F_{14}COO^{\bullet\,-} + F^{-} \tag{9}$$

$$C_7F_{14}COO^{\bullet\,-} + H_2O \rightarrow C_7F_{14}HCOO^{-} + OH^{\bullet} \tag{10}$$

$\rightarrow\rightarrow\rightarrow C_7F_9H_6COO^-$, $C_6F_9H_4COO^-$, $C_3F_3H_4COO^-$

3. Recombination of $SO_3^{\bullet\,-}$

$$C_7F_{15}^{\bullet} + SO_3^{\bullet\,-} \rightarrow C_7F_{15}SO_3^{\,-} \tag{11}$$

$$C_6F_{13}^{\bullet} + SO_3^{\bullet\,-} \rightarrow C_6F_{13}SO_3^{\,-} \tag{12}$$

4. Elimination of CF_2

$$C_7F_{15}^{\bullet} + H_2O \rightarrow C_7HF_{15} + OH^{\bullet} \tag{13}$$

$$C_7HF_{15} \rightarrow C_6HF_{13} + CF_2 \tag{14}$$

$$C_6F_{13}^{\bullet} + H_2O \rightarrow C_6HF_{13} + OH^{\bullet} \tag{15}$$

$$C_6HF_{13} \rightarrow C_5HF_{11} + CF_2 \tag{16}$$

Table S1. The composition of two real groundwaters.

Source	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Initial pH
GW1	5.7	1.8	14.2	1.0	29	7.1
GW2	57.7	1.9	65.5	0.8	299	7.5

Table S2. Specific surface area, pore size and pore volume of α-, β-, γ-MnO_2

	Specific surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
α-MnO_2	59.3	15.0	0.22
β-MnO_2	1.7	6.0	0.0025
γ-MnO_2	69.9	14.5	0.25

Table S3. The final pH of PFOS degradation experiments using solutions with different H_2O_2 concentration, γ-MnO_2 loading, initial PFOS concentration, initial pH, Cl- ions addtion, and humic acid addition. Initial pH =7.0 if not specified.

Variable in batch experiment		Final pH
H_2O_2 conc.	0.1 M	8.0
	0.25 M	8.2
	0.5 M	8.3
	1 M	8.1
γ-MnO_2 dose	5 mg/L	7.7
	10 mg/L	7.8
	20 mg/L	8.1
	50 mg/L	9.1
PFOS conc.	0.1 μM	8.3
	0.25 μM	8.1
	0.5 μM	8.1
	1 μM	8.2
Initial pH	3	3.3
	5	7.3
	7	8.1
	9	11.0
Cl^- conc.	0 mg/L	8.1
	5 mg/L	8.0
	50 mg/L	8.0
Humic acid conc.	0 mg/L	8.1
	1 mg/L	8.1
	5 mg/L	7.9

Table S4. Intermediates identified by UHPLC-QTOF-MS.

Compound	Formula	Mass to charge ratio $[M-H]^-$ (m/z)
Target compound		
PFOS	$C_8F_{17}SO_3H$	498.9370
Intermediate (short-chain PFCAs)		
PFOA	$C_7F_{15}COOH$	412.9704
PFHpA	$C_6F_{13}COOH$	362.9744
Intermediate (H-substituted PFCAs)		
BP1	$C_7F_9H_6COOH$	305.0237
BP2	$C_6F_9H_4COOH$	291.0066
BP3	$C_3F_3H_4COOH$	141.0167
Intermediate (Short-chain -PFSAs)		
PFHpS	$C_7F_{15}SO_3H$	448.9314
PFHxS	$C_6F_{13}SO_3H$	398.9405
Intermediate (C_nHF_{2n+1})		
BP4	C_6HF_{13}	318.9786
BP5	C_5HF_{11}	268.9822
Intermediate (Long-chain byproducts)		
BP6	$C_{12}F_{18}H_8O$	509.0162
BP7	$C_6F_9H_5O$	263.0109
BP8	$C_8F_{16}H_2SO_3$	480.9379
BP9	$C_8F_{15}H_3SO_3$	462.9496
BP10	$C_8F_{15}HSO_3$	460.9313

※BP represents byproduct

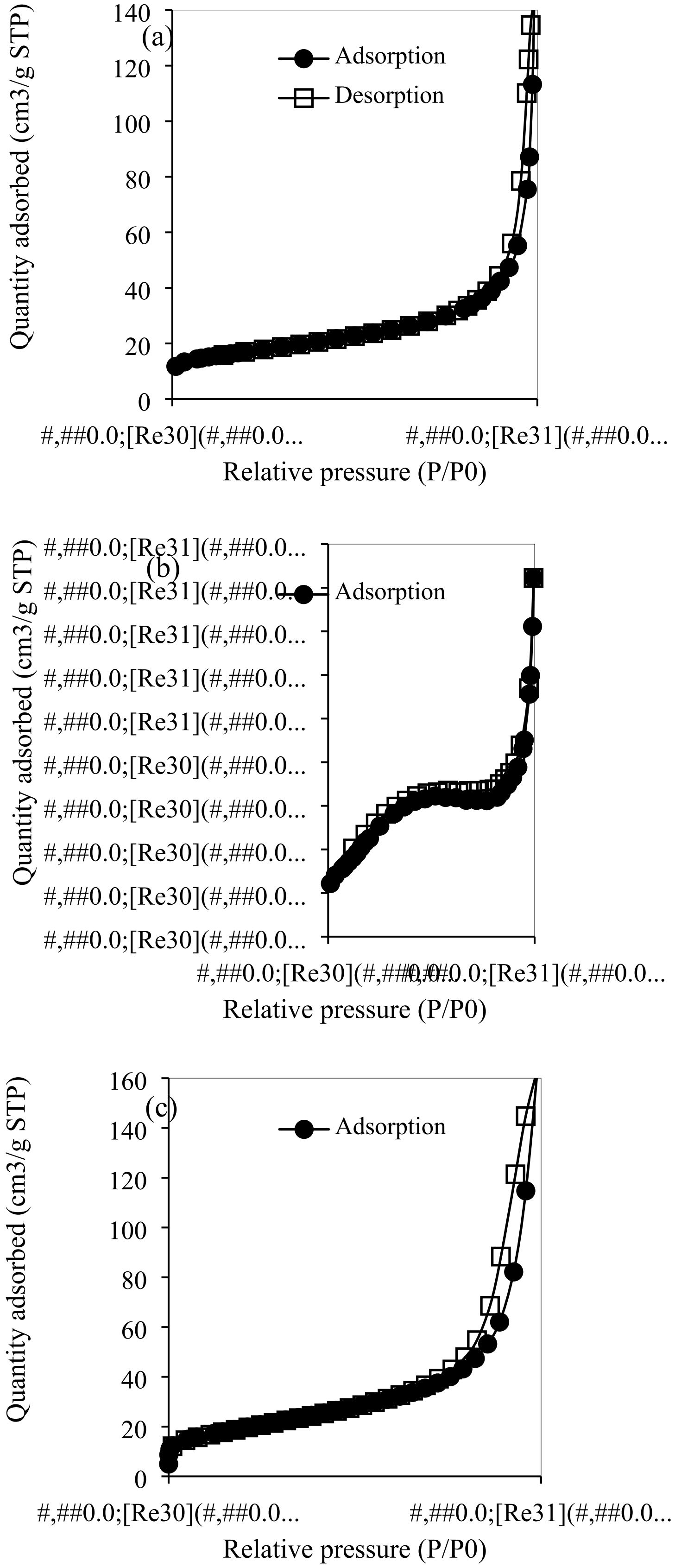

Figure S1. N_2 adsorption-desorption isotherms of (a) α-MnO_2, (b) β-MnO_2, (c) γ-MnO_2.

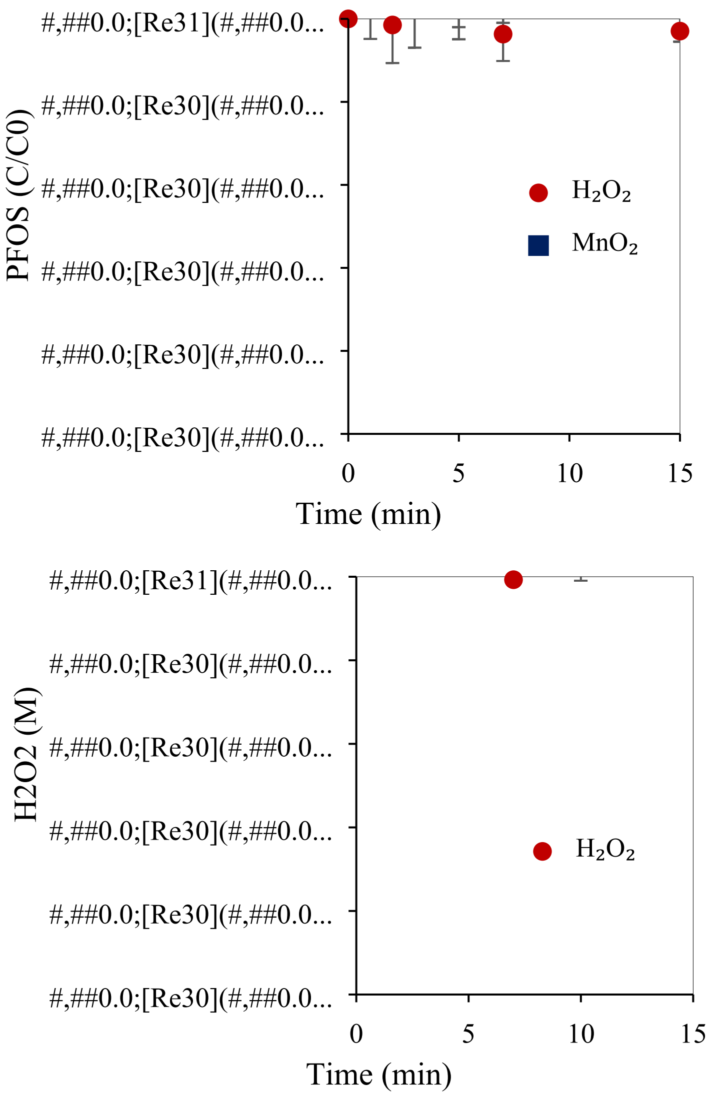

Figure S2. (a) Degradation of PFOS and (b) Decomposition of H_2O_2 in control experiments. Experimental condition: $[H_2O_2]$ = 1 M or MnO_2 loading = 20 mg/L, [PFOS] = 0.25 μM, Initial pH = 7, $[HCO_3^-]$ = 3 mM.

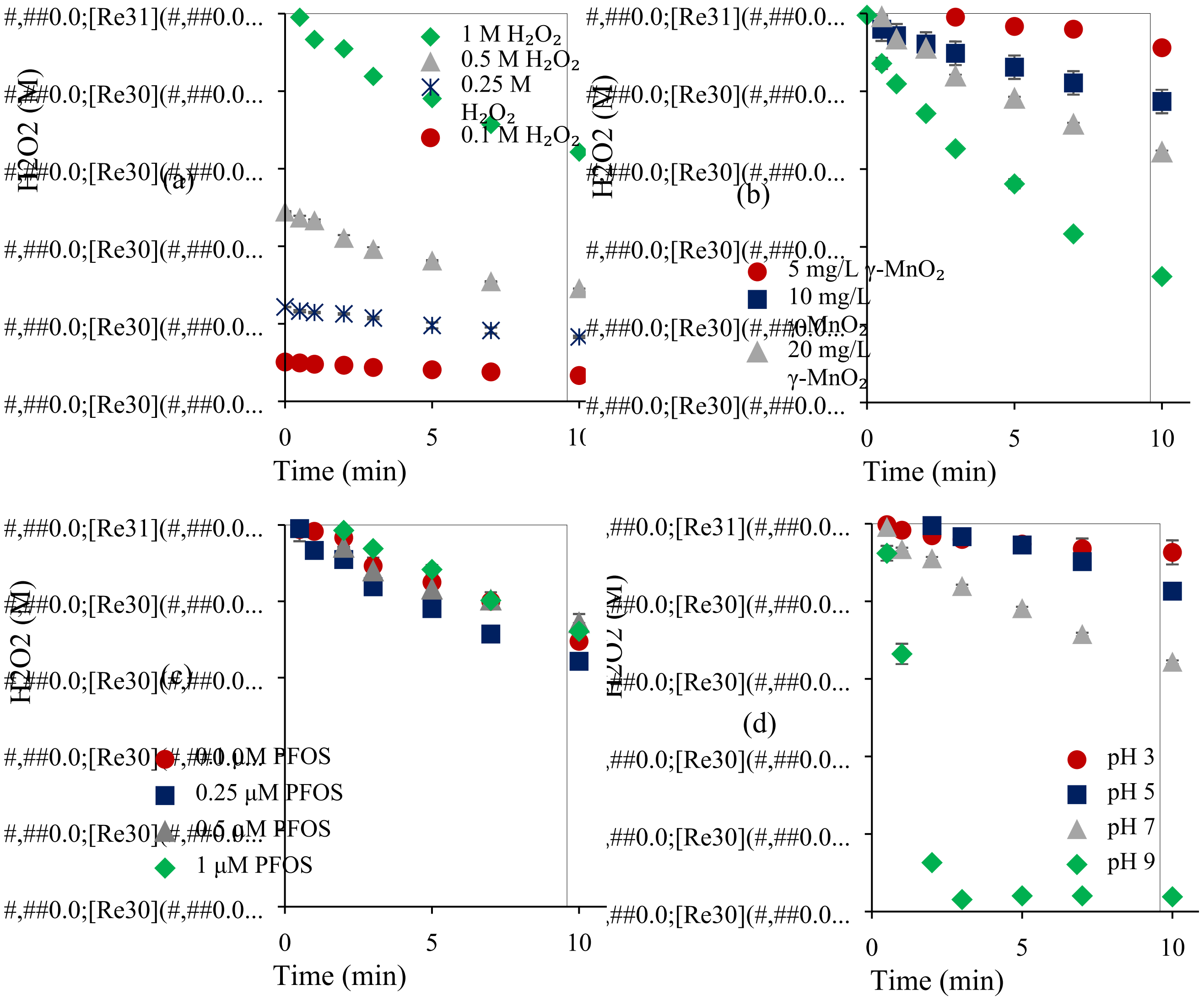

Figure S3. Effects of (a) H_2O_2 concentration, (b) γ-MnO_2 loading, (c) PFOS concentration, (d) Initial pH on the consumption of H_2O_2. Experimental condition: [H_2O_2] = 1 M, MnO_2 loading = 20 mg/L, [PFOS] = 0.25 μM, Initial pH = 7, [HCO_3^-] = 3 mM if not stated otherwise

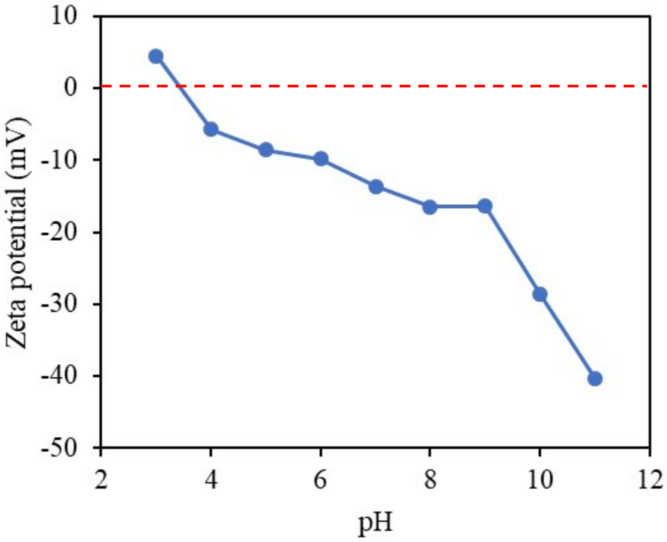

Figure S4. Determination of pH_{pzc} of γ-MnO_2.

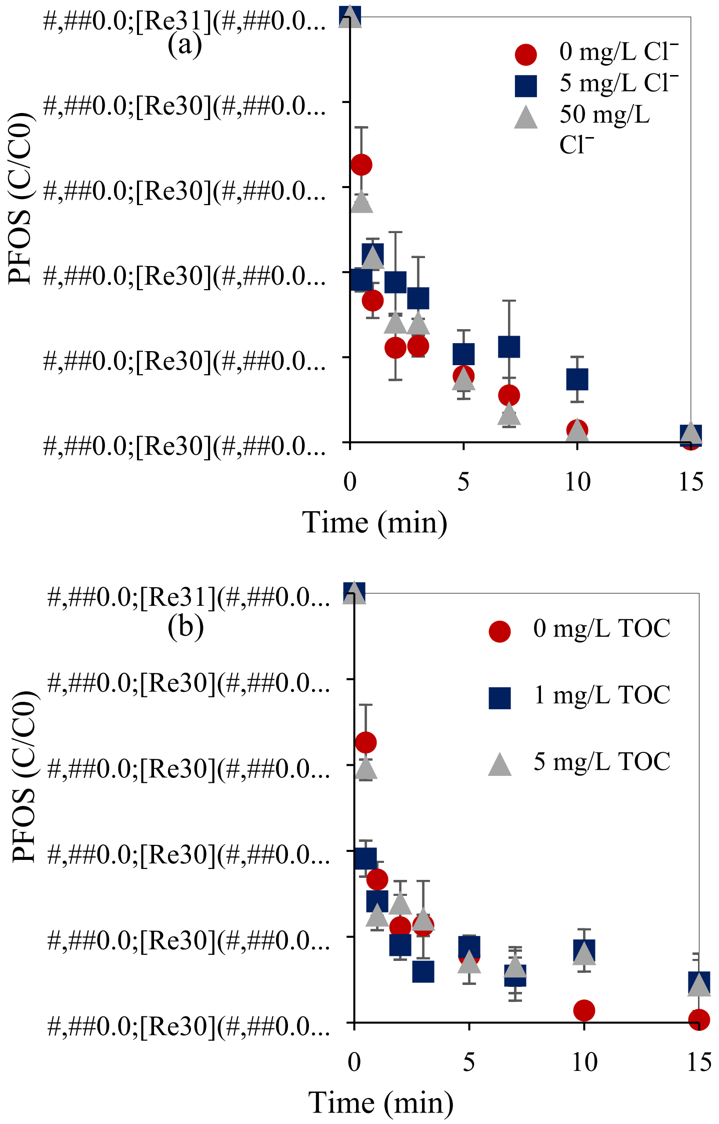

Figure S5. Effects of (a) chloride and (b) humic acid (expressed as TOC) on PFOS degradation. Experimental condition: [H_2O_2] = 1 M, MnO_2 loading = 20 mg/L, [PFOS] = 0.25 μM, Initial pH = 7, [HCO_3^-] = 3 mM.

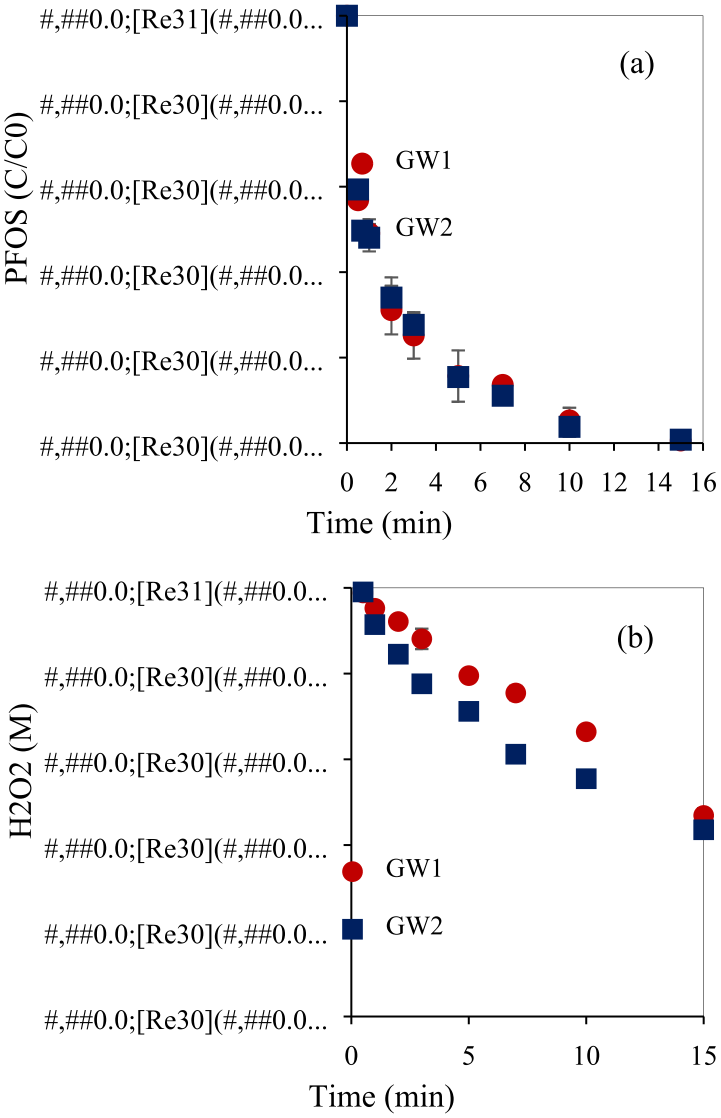

Figure S6. (a) Degradation of PFOS and (b) decomposition of H_2O_2 in two real groundwaters. Experimental condition: $[H_2O_2]$ = 1 M, MnO_2 loading = 20 mg/L, [PFOS] = 0.25 μM.

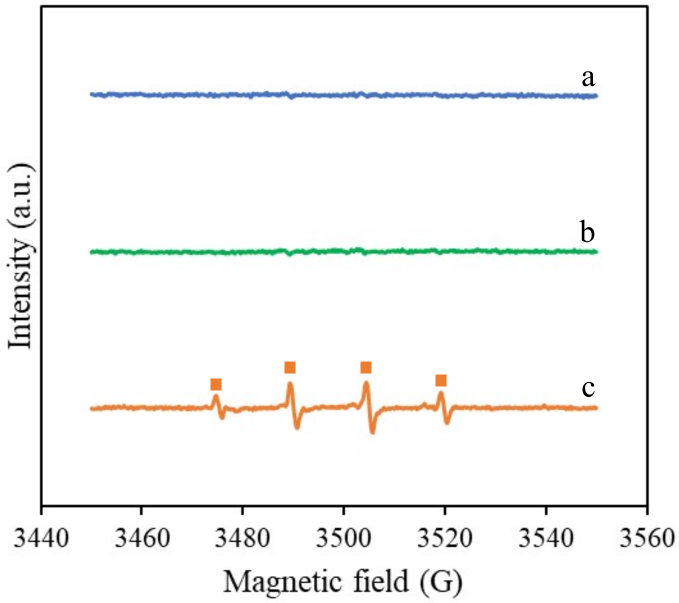

Fig S7. EPR spectra of (a) DI water, (b) DI water with HCO_3^-, and (c) DI water with HCO_3^- and H_2O_2. Experimental condition: [DMPO] = 0.5 M, pH = 7. If present, [HCO_3^-] = 3 mM, [H_2O_2] = 1 M. ■=DMPO-OH.