-Supporting Information-

First assessment on degradability of OBS, a high volume alternative to PFOS in fire-fighting foams and oil production agents in China

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Section S1 Calculation of biodegradation efficiency during CBT for OBS

Based on the OECD Guideline 301D Closed Bottle Test (CBT)[1], the theoretical oxygen demand (ThOD) is calculated on the basis of elemental composition. Thus, for the compound: $C_cH_hCl_{cl}N_nNa_{na}O_oP_pS_s$,

the ThOD, without nitrification, would be:

$$ThOD_{NH_3} = \frac{16 \times [2c + \frac{1}{2}(h - cl - 3n) + 3s + \frac{5}{2}p + \frac{1}{2}na - o]}{MW} mg/mg \quad \text{(S-1)}$$

where MW is the molecular weight.

For OBS: $C_{15}H_5F_{17}O_4SNa$,

$$ThOD_{NH_3} = \frac{16 \times [2 \times 15 + \frac{1}{2} \times (5 - 17) + 3 + \frac{1}{2} - 4]}{627} = 0.599 mg/mg \quad \text{(S-2)}$$

For reference substance, sodium benzoate: $C_7H_5O_2Na$,

$$ThOD_{NH_3} = \frac{16 \times [2 \times 7 + \frac{1}{2} \times 5 + \frac{1}{2} - 2]}{144} = 1.667 mg/mg \quad \text{(S-3)}$$

Calculate the percentage biodegradation by dividing the specific BOD by the specific ThOD. The BOD exerted after each time period was calculated by subtracting the oxygen depletion (mg O_2/L) of the inoculum blank from that exhibited by the test substance. Thus:

$$BOD = \frac{mg\ O_2/L\ up\ take\ by\ test - mg\ O_2/L\ uptake\ by\ blank}{mg\ test\ substance/L\ in\ vessel} \quad \text{(S-4)}$$

And

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[1]Organisation for Economic Cooperation and Development (OECD), Guidelines for Testing of Chemicals (301D, closed bottle test), **1992**. http://www.oecd-ilibrary.org/test-no-301-ready-biodegradability_5lmqcr2k7qmw.pdf?contentType=/ns/Book&itemId=/content/book/9789264070349-en&containerItemId=/content/serial/2074577x&accessItemIds=&mimeType=application/pdf.

$$\%\ Degradation = \frac{BOD\ (mg\ O_2/mg\ test\ substance)}{ThOD\ (mg\ O_2/mg\ test\ substance)} \times 100 \quad \text{(S-5)}$$

Section S2 Photochemical experiment under 365 nm

The photochemical reaction of OBS under 365 nm was performed in reactor equipped with simulated sunlight source (xenon lamp, PLS SXE300C, Beijing Bofeilai Science and Technology Ltd.), the current was set as 15 A and 365 nm band-pass filter was used to control the wavelength exposed on OBS solution.

Table S1 Retention time and optimized quantification parameters for PSA and TFA.

Substances	Retention time (min)	Parent ion (Da)	Daughter ions (Da)	CE (volts)	DP (volts)	EP (volts)	CEP (volts)	CXP (volts)
PSA	2.5	172.700	80.000 93.000 106.000	-37.000	-40.000	-5.000	-8.000	-1.500
TFA	2.7	112.988	69.000	-14.000	-18.000	-1.000	-8.000	-1.000

Note: The collision energy (CE), decluster potential (DP), entrance potential (EP), collision entrance potential (CEP) and collision exit potential (CXP).

Table S2 Consumption of DO in CBT during 28 days.

Days	Blank（mg/L）			Reference group（mg/L）			OBS（mg/L）		
	Bottles1	Bottles2	Average	Bottles1	Bottles2	Average	Bottles1	Bottles2	Average
0	8.99	9.03	9.01	9.06	9.11	9.085	9.07	9.07	9.07
4	8.96	8.84	8.90	4.76	4.88	4.82	8.80	8.83	8.815
7	8.85	8.91	8.88	4.88	3.80	4.34	8.98	8.74	8.86
11	8.75	8.75	8.75	3.33	3.62	3.475	8.75	8.76	8.755
14	8.68	8.64	8.66	3.39	4.35	3.87	8.69	8.71	8.70
18	8.69	8.63	8.66	3.09	3.19	3.14	8.63	8.48	8.555
21	8.76	8.72	8.74	3.00	3.36	3.18	8.82	8.92	8.87
25	8.49	8.51	8.50	3.95	3.04	3.495	8.54	8.52	8.53
27	8.49	8.47	8.48	2.85	3.13	2.99	8.48	8.52	8.50
28	8.41	8.43	8.42	3.40	3.56	3.48	8.48	8.69	8.585

Table S3 Biodegradation efficiency of OBS in CBT during 28 days.

	Average degradation efficiency after n days（%）									
Days	0	4	7	11	14	18	21	25	27	28
Reference substance	0	62.20	69.09	80.09	72.83	83.76	84.36	76.05	83.31	75.07
OBS	0	3.07	1.69	1.17	0.42	3.50	0	0.64	0.85	0

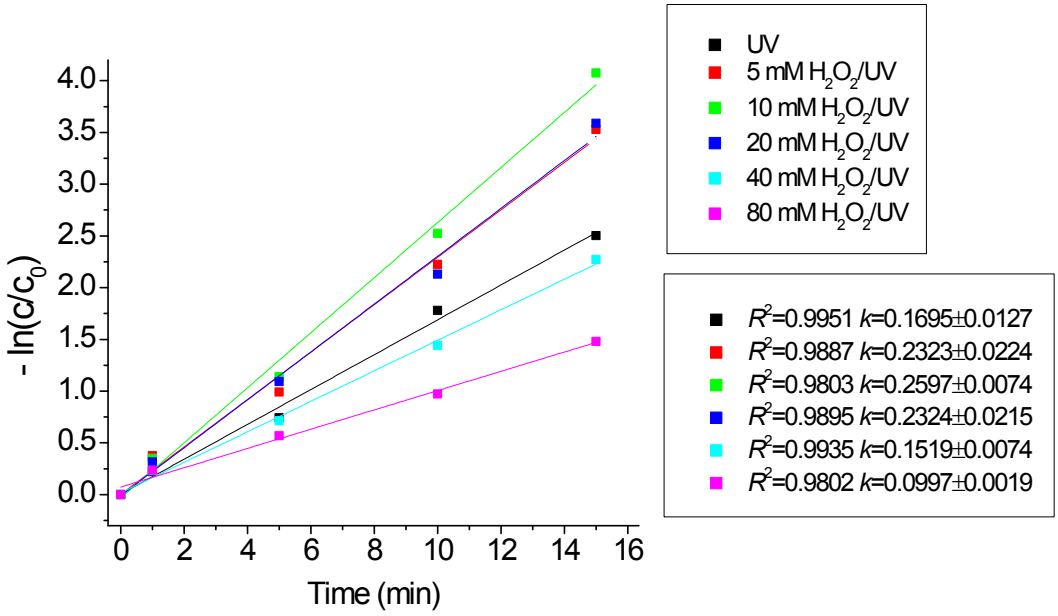
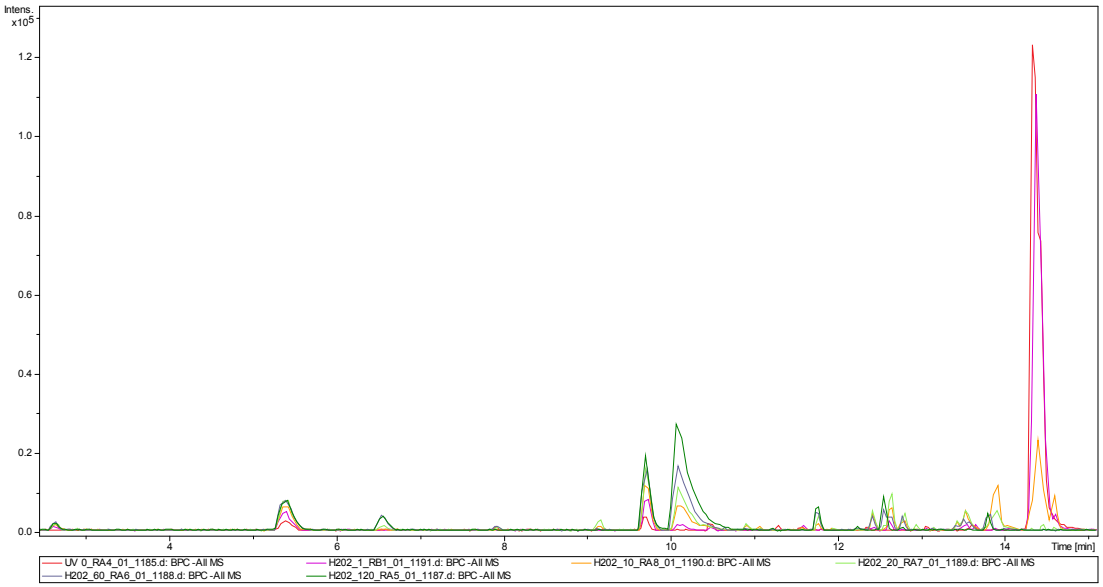
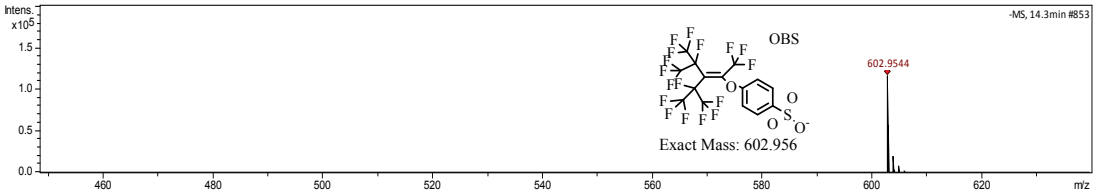


Fig. S1 Pseudo- first order kinetic fitting curve for degradation of OBS under UV with varied dose of H_2O_2.


Intens.
x10^5
Time [min]
UV 0_RA4_01_1185.d: BPC -All MS
H202_1_RB1_01_1191.d: BPC -All MS
H202_10_RA8_01_1190.d: BPC -All MS
H202_20_RA7_01_1189.d: BPC -All MS
H202_60_RA6_01_1188.d: BPC -All MS
H202_120_RA5_01_1187.d: BPC -All MS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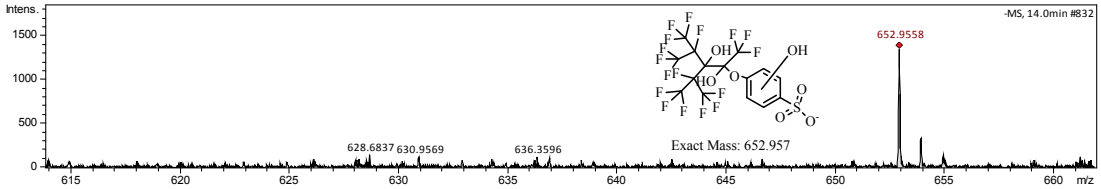
OBS
602.9544
Exact Mass: 602.956
m/z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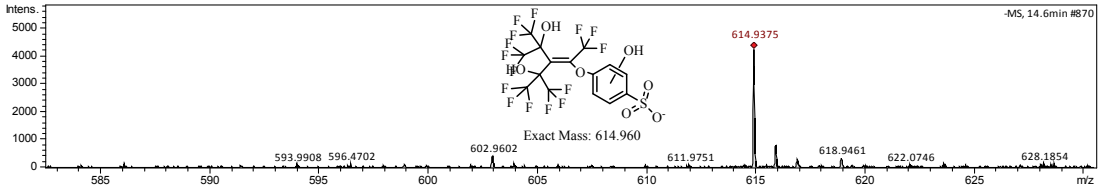
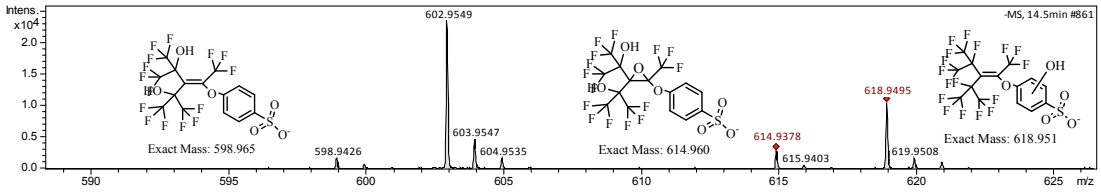
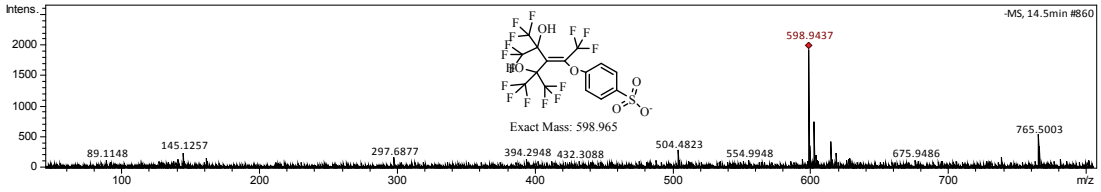
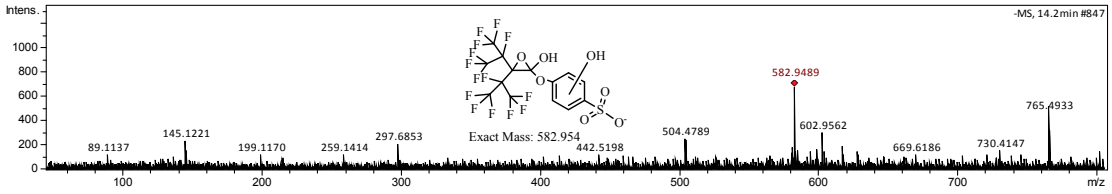
652.9558
628.6837
630.9569
636.3596
Exact Mass: 652.957
m/z


-MS, 14.6min #870
614.9375
593.9908
596.4702
602.9602
611.9751
618.9461
622.0746
628.1854
Exact Mass: 614.960
m/z


-MS, 14.5min #861
602.9549
603.9547
604.9535
598.9426
Exact Mass: 598.965
614.9378
615.9403
Exact Mass: 614.960
618.9495
619.9508
Exact Mass: 618.951
m/z


-MS, 14.5min #860
598.9437
89.1148
145.1257
297.6877
394.2948
432.3088
504.4823
554.9948
675.9486
765.5003
Exact Mass: 598.965
m/z


-MS, 14.2min #847
582.9489
89.1137
145.1221
199.1170
259.1414
297.6853
442.5198
504.4789
602.9562
669.6186
730.4147
765.4933
Exact Mass: 582.954
m/z

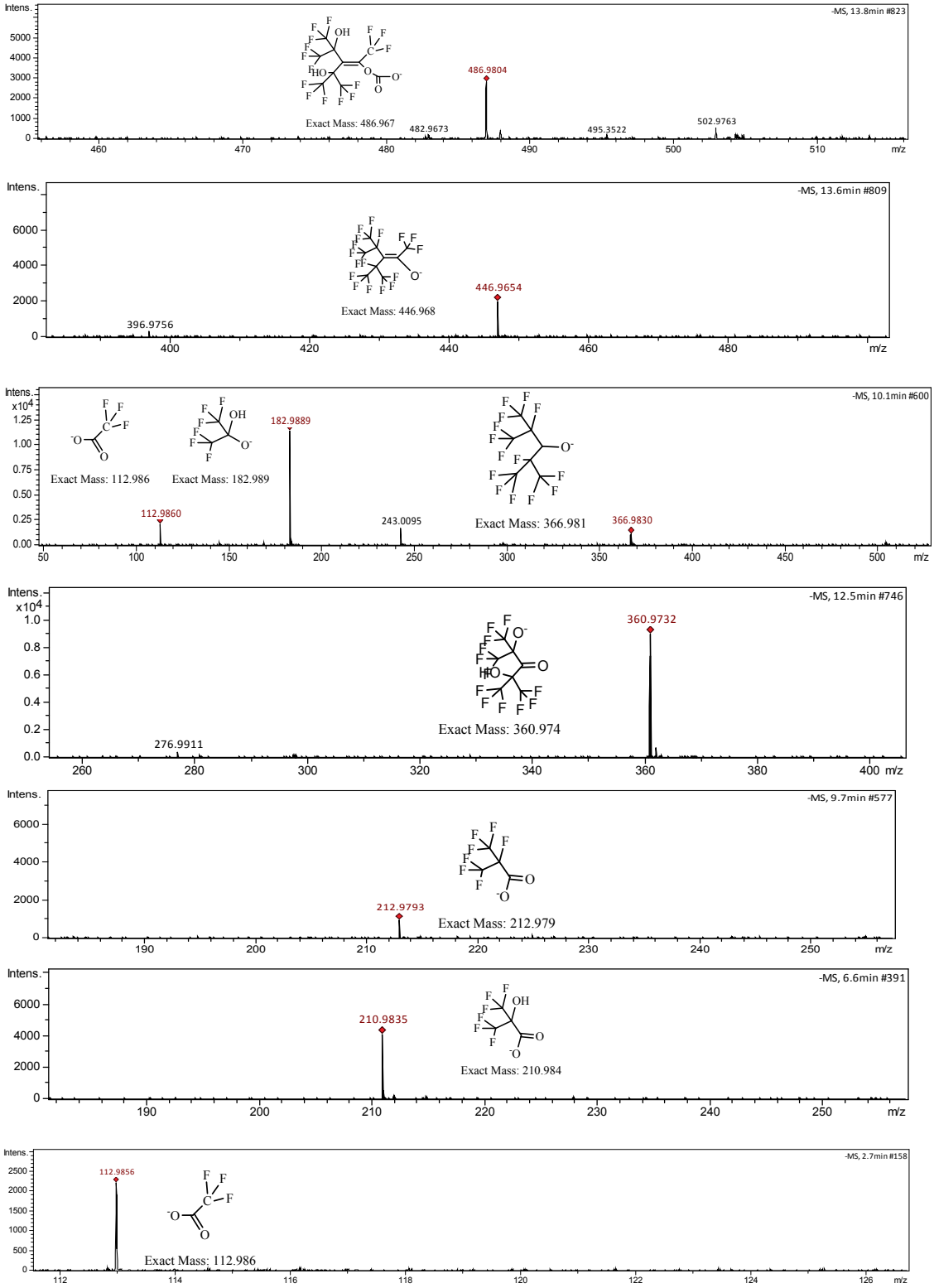


Fig. S2 Products derived from the degradation of OBS under UV/H_2O_2

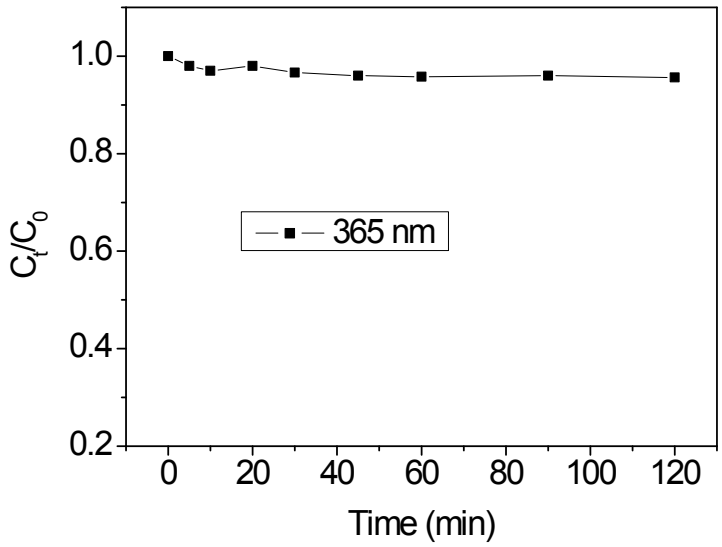


Fig. S3 Variation of OBS concentration under UV (365 nm) in 2 hours.

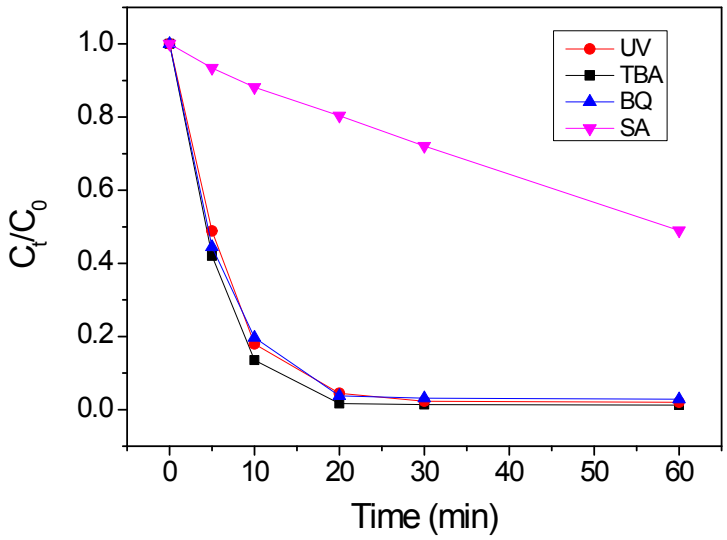
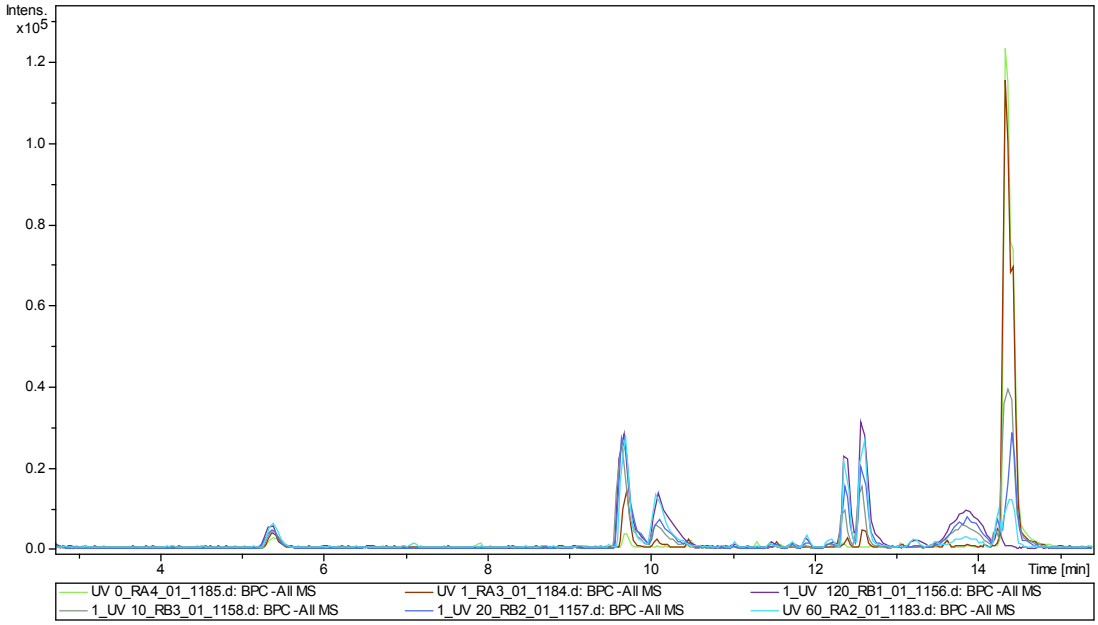
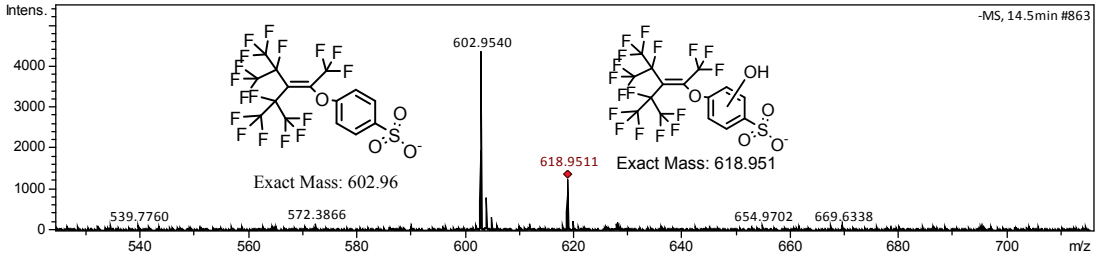
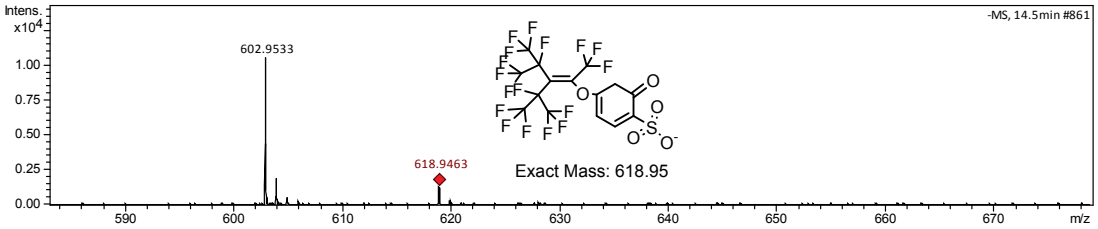
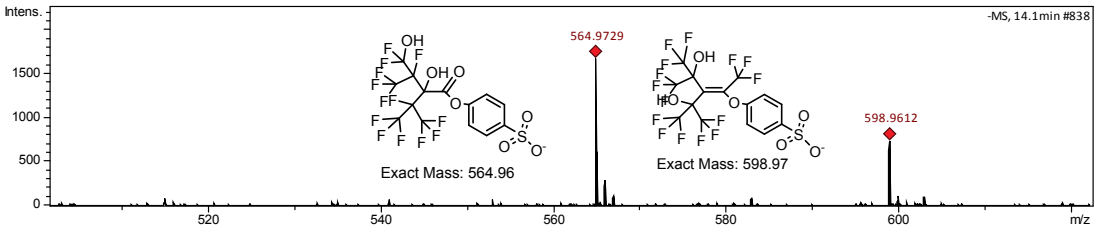


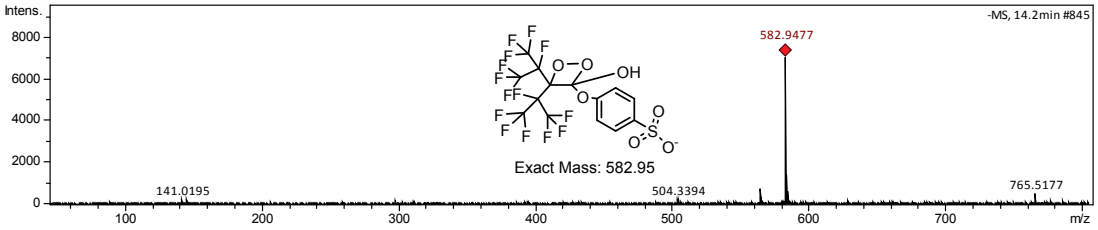
Fig. S4 Inhibition of degradation of OBS by TBA (for OH•), BQ (for O_2•$^-$), SA (for $^1O_2$ and OBS*).

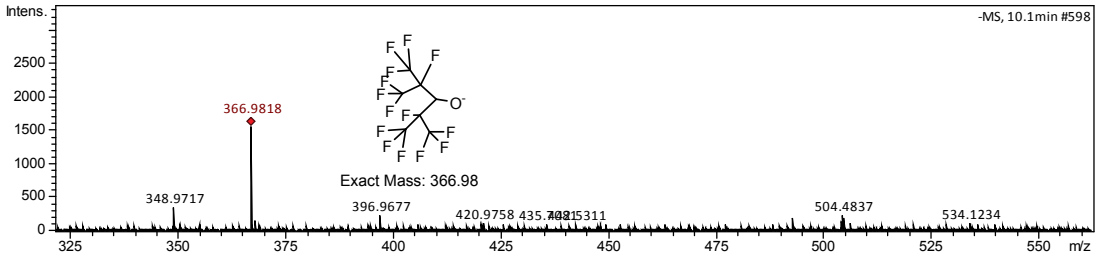

Intens.
x10^5
1.2
1.0
0.8
0.6
0.4
0.2
0.0
4
6
8
10
12
14
Time [min]
UV 0_RA4_01_1185.d: BPC -All MS
UV 1_RA3_01_1184.d: BPC -All MS
1_UV 120_RB1_01_1156.d: BPC -All MS
1_UV 10_RB3_01_1158.d: BPC -All MS
1_UV 20_RB2_01_1157.d: BPC -All MS
UV 60_RA2_01_1183.d: BPC -All MS

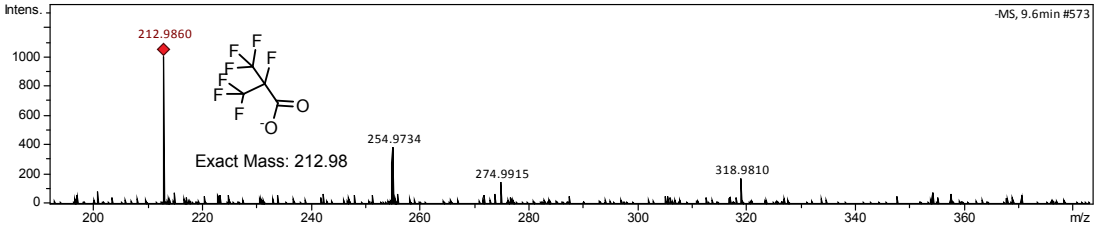

Intens.
-MS, 14.5min #863
602.9540
618.9511
Exact Mass: 602.96
Exact Mass: 618.951
539.7760
572.3866
654.9702
669.6338
4000
3000
2000
1000
0
540
560
580
600
620
640
660
680
700
m/z

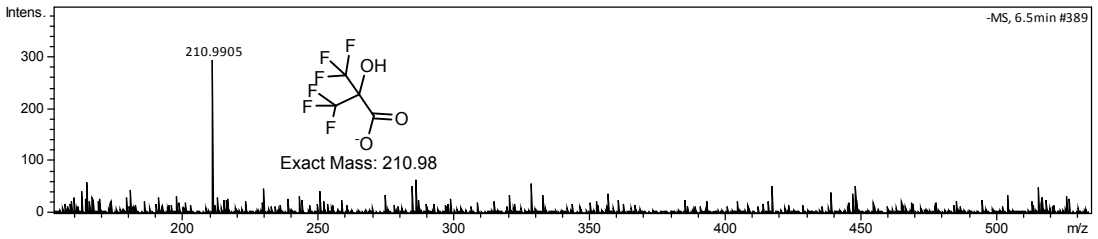

Intens.
x10^4
-MS, 14.5min #861
602.9533
618.9463
Exact Mass: 618.95
1.00
0.75
0.50
0.25
0.00
590
600
610
620
630
640
650
660
670
m/z


Intens.
-MS, 14.1min #838
564.9729
598.9612
Exact Mass: 564.96
Exact Mass: 598.97
1500
1000
500
0
520
540
560
580
600
m/z


Intens.
-MS, 14.2min #845
582.9477
Exact Mass: 582.95
141.0195
504.3394
765.5177
8000
6000
4000
2000
0
100
200
300
400
500
600
700
m/z


Intens.
-MS, 10.1min #598
366.9818
348.9717
396.9677
420.9758
504.4837
534.1234
Exact Mass: 366.98
m/z


Intens.
-MS, 9.6min #573
212.9860
254.9734
274.9915
318.9810
Exact Mass: 212.98
m/z


Intens.
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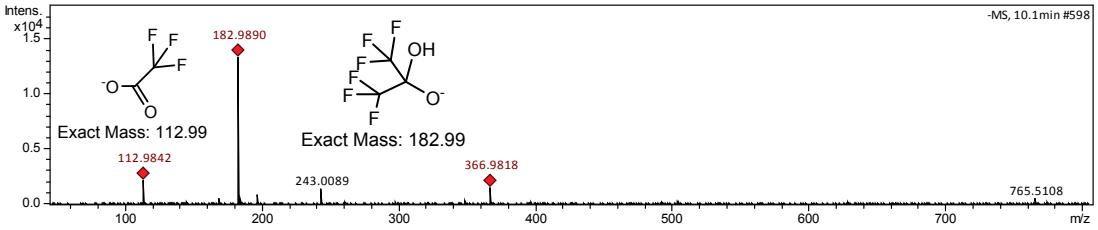
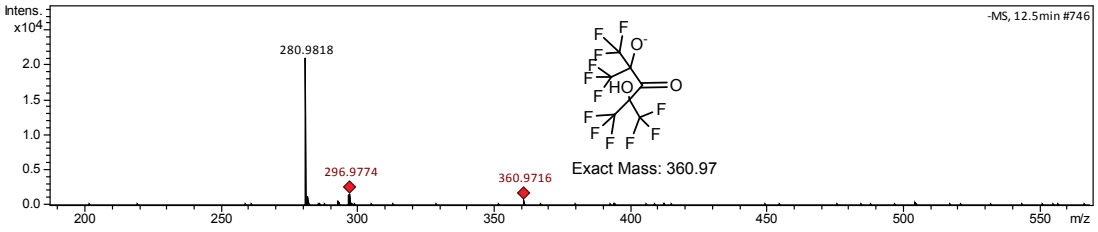
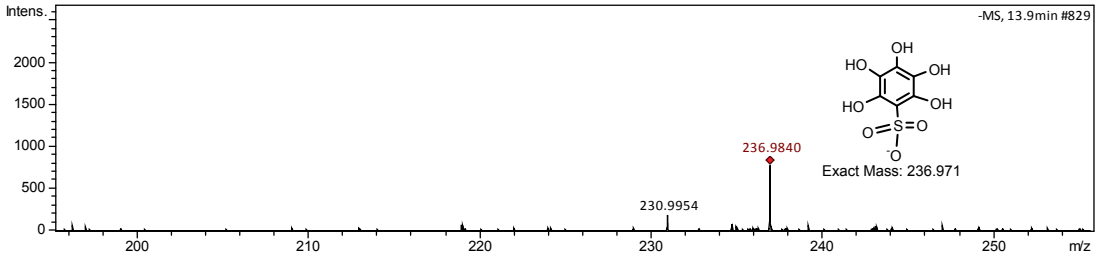
210.9905
Exact Mass: 210.98
m/z


Intens.
x10^4
-MS, 10.1min #598
182.9890
112.9842
243.0089
366.9818
765.5108
Exact Mass: 112.99
Exact Mass: 182.99
m/z


Intens.
x10^4
-MS, 12.5min #746
280.9818
296.9774
360.9716
Exact Mass: 360.97
m/z


Intens.
-MS, 13.9min #829
236.9840
230.9954
Exact Mass: 236.971
m/z

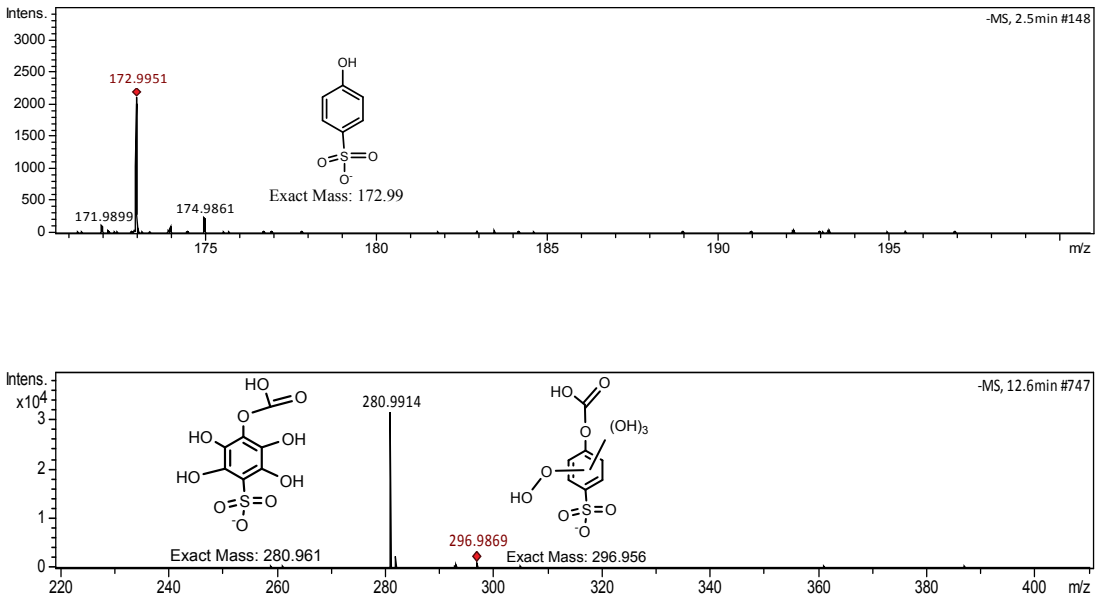


Fig. S5 Products derived from the degradation of OBS under UV irradiation.

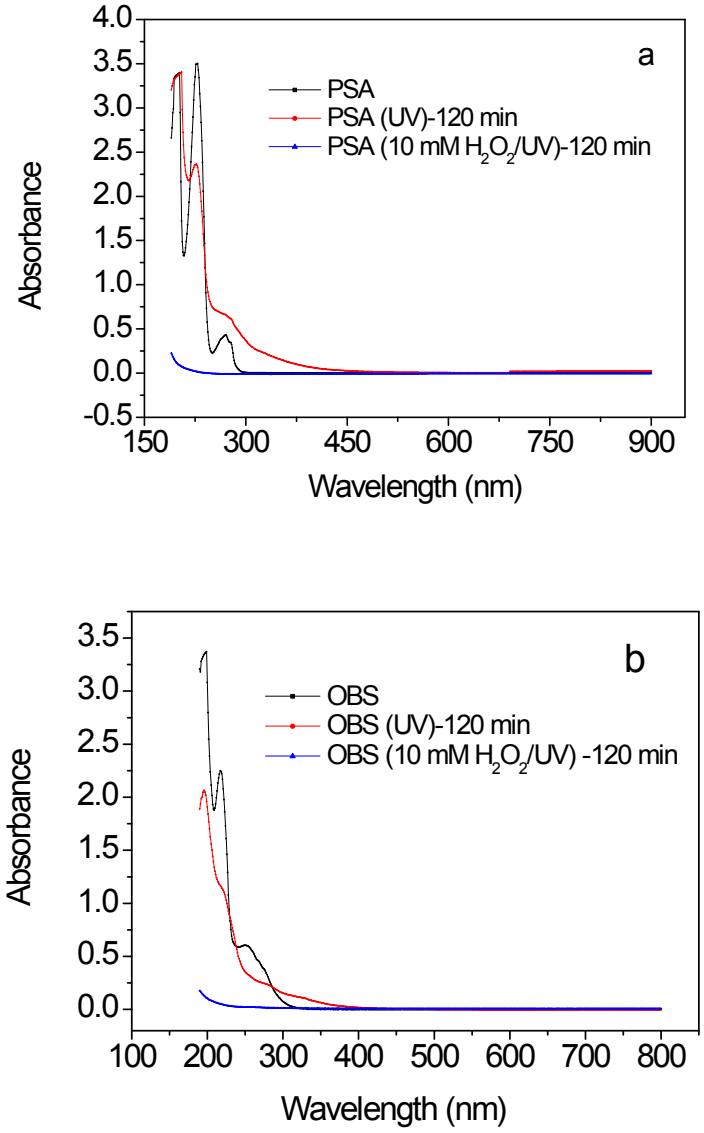


Fig. S6 UV-Vis absorption spectra of PSA aqueous solution (PSA: 0.16 mM) (a) and OBS aqueous solution (OBS: 0.16 mM) (b) under UV and UV/H_2O_2 system before and after 2 h reaction.

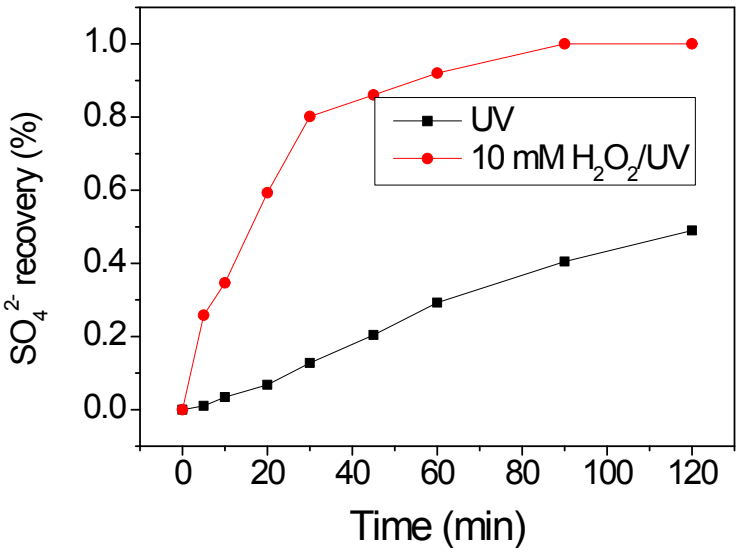


Fig. S7 Sulfate ion recovery ratio for PSA in UV and UV/H_2O_2 system.