Supporting Information

Text S1

A 50 L water sample was on each occasion and filtered through a 0.45 μm glass fiber filter (GF/F, Merck Millipore, USA). The filtered sample was then enriched and concentrated by reverse osmosis through a 300 Da membrane (BONA-GM-19, Jinan, China). The concentrated samples were freeze-dried and ground to powder, and then placed in brown glass bottles. The dewatered sludge was dried and mixed with ultrapure water (resistance > 18.2 MΩ·cm) and the supernatant of the suspension was collected for repeated reverse osmosis to extract the DOM from the sludge.

Text S2

FTIR spectroscopy (Varian 640-IR, USA) using the KBr pellet technique. DOM (5.0 mg C/L) was diluted with 0.01 mol/L KCl solution to pH 6.0. The solutions were scanned over the range of 200–700 nm with a UV-visible spectrometer (UV-2600, Shimadzu, Japan), and scanned using an F-7000 spectrophotometer (F-7000, Hitachi Limited, Japan) with a bandpass slit width of 5 nm for both the excitation and emission (the scanning ranges were 200–600 nm) at a scanning speed of 2400 nm/min.

The detections of $^1O_2$ and •OH in the 5 mg C/L DOM solutions were examined by 100 mmol/L of 2,2,6,6-tetramethyl-4-piperidone (TEMP) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), respectively. After illumination, the reaction solutions were then quantified using an EPR spectrometer (Bruker A300, Germany). The details were as follows: a center magnetic field of 3510 G, a sweep width of 100 G, microwave frequency 9.87 GHz and microwave power 20.00 mW.

The residual concentration of FFA can be determined by a high-performance liquid chromatograph (HPLC 1260 series, Agilent, USA). The mobile phase was 20% acetonitrile and 80% ultrapure water, both containing 0.1% trifluoroacetic acid. The flow rate was 1 mL/min. The detection wavelength was 218 nm, and the injection volume was 50 μL.

The formation concentration of 2h-TPA was detected by three-dimension excitation emission matrix fluorescence spectroscopy (3D-EEMs, F-7000, Hitachi Limited, Japan) with a bandpass slit width of 5 nm at a scanning speed of 2400 nm/min (excitation wavelength 315 nm; emission wavelength 425 nm).

Liquid chromatograph mass spectrometer (LC-MS, Shimadzu 8045, Japan) was used to characterize the products and by-products of EE2 in the photodegradation system after 5 h of treatment. The separation was on a C18 chromatographic column (150 mm × 3.0 mm, 2.7 μm) with a flow rate of 0.4 mL/min, a column temperature of 40℃, and the mobile phase composed of water with 0.1% formic acid and acetonitrile. The gradient was shown in Table S3, and the system was stopped after 14 min. An electrospray ion source on the mass spectrometer performed a full scan of positive ions at a spray voltage of 4000 V with the atomization airflow at 3.0 L/min, a

dryer flow rate of 10.0 L/min, a flow rate of 10.0 L/min, a heating module temperature of 400℃, a tube temperature of 250℃, and an interface temperature at 300℃.

Table S1 The photodegradation rate constants of FFA and the formation rate constants of 2h-TPA in different DOM solutions (k_{obs} (h^{-1})).

Compound	WW1			WW3			WW4			WW8		
	SE_{DOM}	AE_{DOM}	DS_{DOM}	SE_{DOM}	AE_{DOM}	DS_{DOM}	SE_{DOM}	AE_{DOM}	DS_{DOM}	SE_{DOM}	AE_{DOM}	DS_{DOM}
FFA	0.151	0.155	0.073	0.134	0.155	0.040	0.159	0.143	0.040	0.178	0.169	0.047
2h-TPA	0.358	0.214	0.105	0.347	0.188	0.087	0.375	0.201	0.086	0.385	0.209	0.076

Table S2 HPLC parameters for FFA and EE2 detection.

Chemicals	Mobile phase (%)		Flow Rate	Wavelength of Detector (nm)		Injection
	Acetonitrile	Ultrapure water	(mL/min)	UV	FLR(Ex/Em)	volume (μL)
FFA	20	80	1	218	–	50
EE2	60	40	1	–	236/310	40

Table S3 Gradient elution conditions of liquid chromatography.

Time (min)	0.1% Formic acid solution (%)	Acetonitrile (%)
0	92	8
2.5	65	35
5	20	80
6.5	2	98
11	2	98
11.2	92	8
14	92	8

Table S4 The physicochemical properties of DOM.

WWTPs	Treatment process	DOM	Optical indicators			
			$SUVA_{254}$	α280	E_2/E_3	FI
WW1	OD	SE_{DOM}	3.3	28.1	5.8	5.8
		AE_{DOM}	3.5	29.0	6.1	6.1
		DS_{DOM}	2.6	25.3	2.5	2.5
WW3	3AMBR	SE_{DOM}	2.9	24.9	5.3	5.8
		AE_{DOM}	3.3	27.9	5.8	5.3
		DS_{DOM}	1.9	19.3	1.9	1.9
WW4	ICEAS	SE_{DOM}	3.7	32.2	5.3	5.3
		AE_{DOM}	3.5	30.6	5.2	5.2
		DS_{DOM}	1.0	10.1	4.4	4.4
WW8	A^2/O	SE_{DOM}	3.5	30.9	6.2	6.2
		AE_{DOM}	3.6	30.4	6.0	6.0
		DS_{DOM}	1.1	9.9	6.9	4.9

Table S5 Photodegradation rate constants and removal rates of EE2 in WW8-DOM solutions.

Solution	Degradation rate (%)	Apparent rate constant ($\times 10^{-2}$ h^{-1})	Half-life (h)
Ultrapure water	6.23	1.63	42.52
Oxi-WSOM	47.40	12.41	5.59
Ano-WSOM	43.72	11.12	6.23
Ana-WSOM	44.46	11.59	5.98
Oxi-EPS	22.70	4.93	14.06
Ano-EPS	24.40	5.54	12.51
Ana-EPS	34.36	5.99	11.57
Oxi-HA	19.94	4.65	14.91
Ano-HA	22.85	4.72	16.50
Ana-HA	20.29	4.64	14.94
Oxi-FA	34.36	5.99	11.57
Ano-FA	28.24	6.01	11.53
Ana-FA	21.47	5.80	11.95

Table S6 The contribution of PPRI to the photodegradation of EE2 by WW8-DOM.

Sample	$R_{[\bullet OH]}$ (%)	$R_{^1O_2}$ (%)	$R_{^3DOM^*}$ (%)
Oxi-WSOM	1.72	4.40	54.62
Ano-WSOM	2.09	4.68	51.26
Ana-WSOM	2.97	8.86	47.62
Oxi-EPS	2.47	8.72	34.48
Ano-EPS	2.75	7.94	36.10
Ana-EPS	1.78	5.51	44.41
Oxi-HA	2.76	11.61	13.97
Ano-HA	0.99	13.35	14.62
Ana-HA	1.51	8.62	12.07
Oxi-FA	1.23	13.69	21.37
Ano-FA	0.99	26.62	26.12
Ana-FA	0.94	25.34	19.31

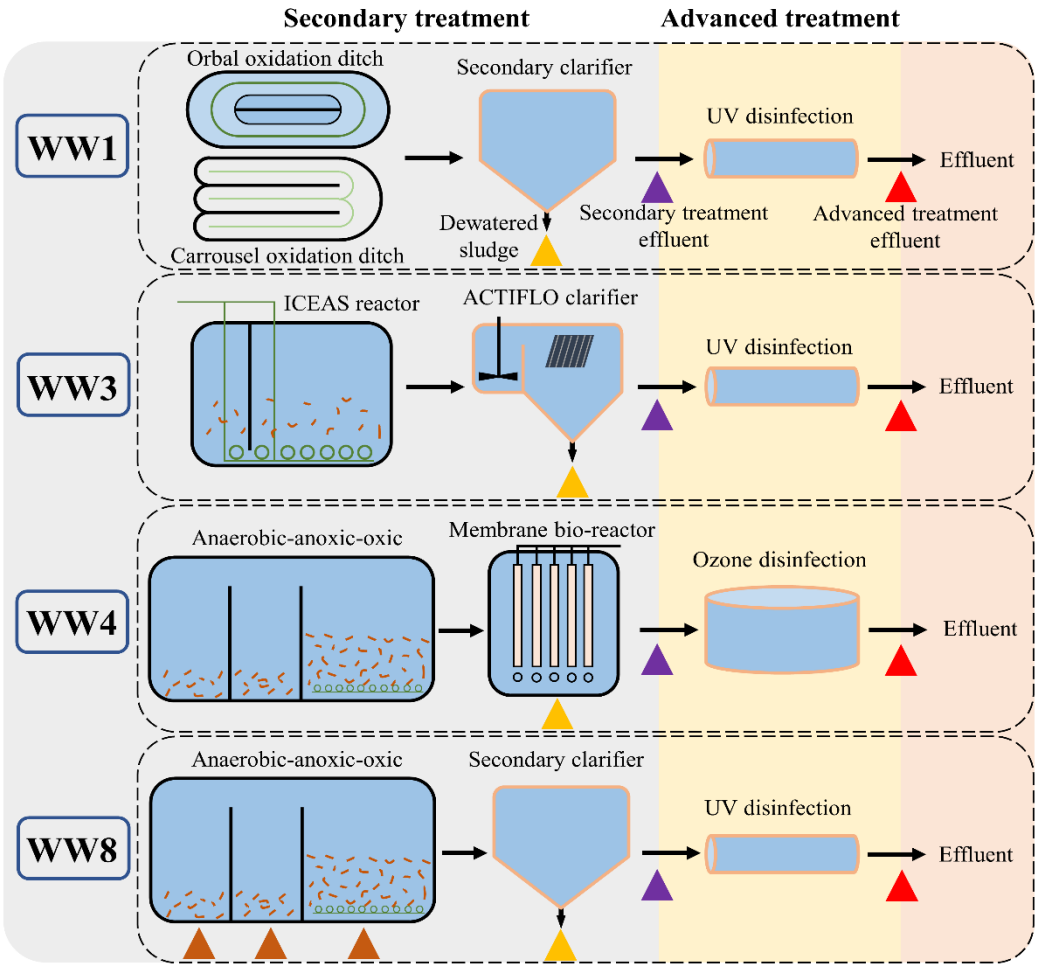

Fig. S1 The sampling sites in four typical WWTPs. The triangles represent the sampling sites in each treatment process.

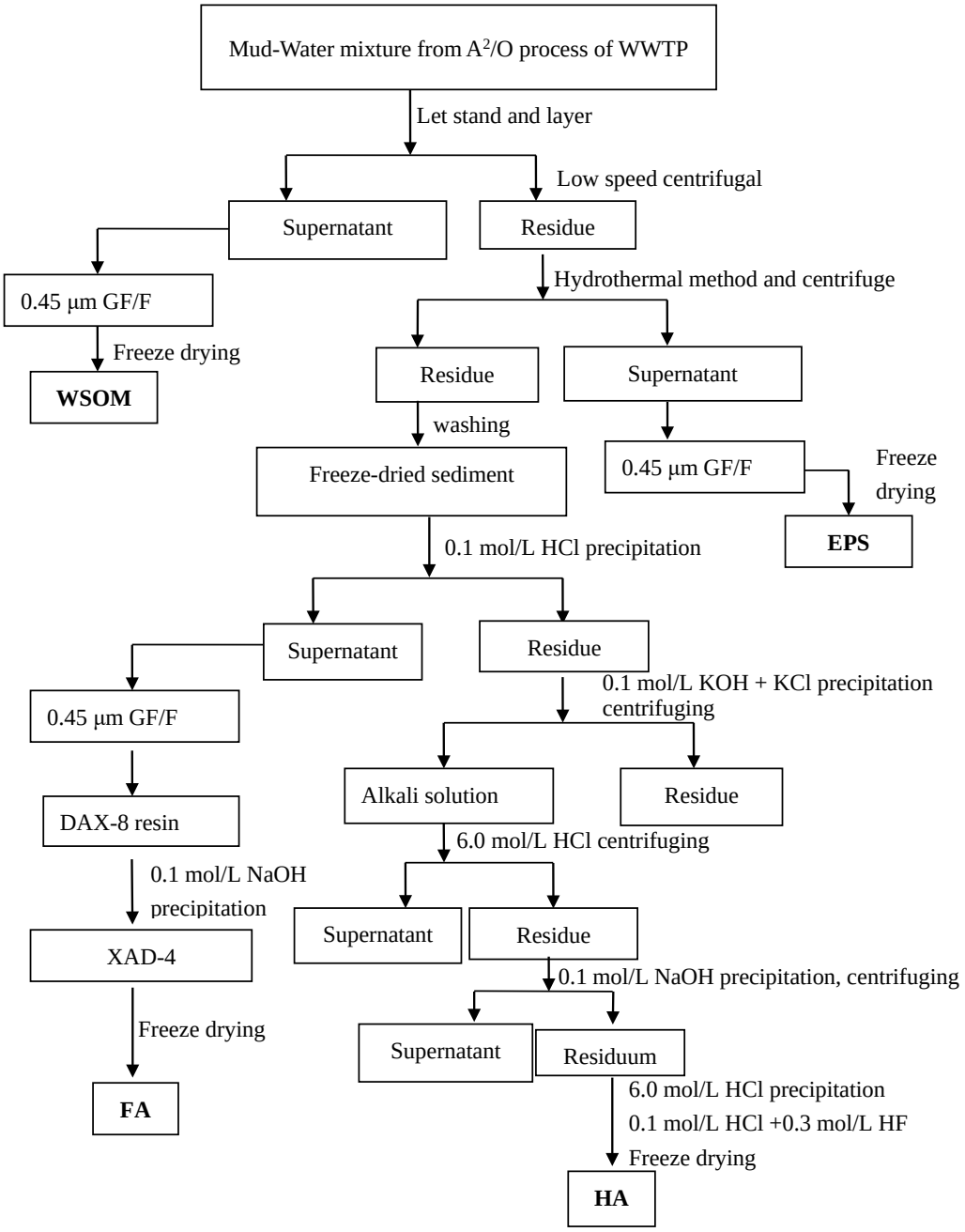

Fig. S2 The extraction process diagram of WSOM, EPS, HA, and FA from A^2/O process.

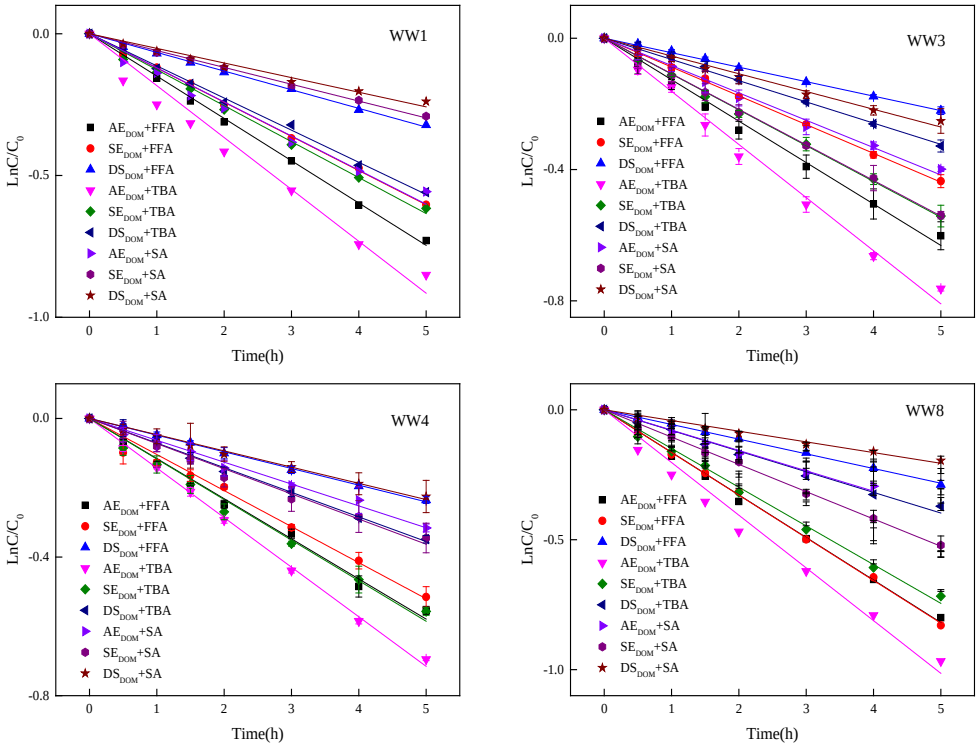

Fig. S3 The photodegradation of EE2 in DOM solutions with the addition of different reactive species scavengers. Reaction conditions: [EE2] = 0.5 mg/L, [DOM] = 5 mg C/L, [FFA] = 40 μmol/L, [TBA] = 30 μmol/L, [SA] = 20 μmol/L.

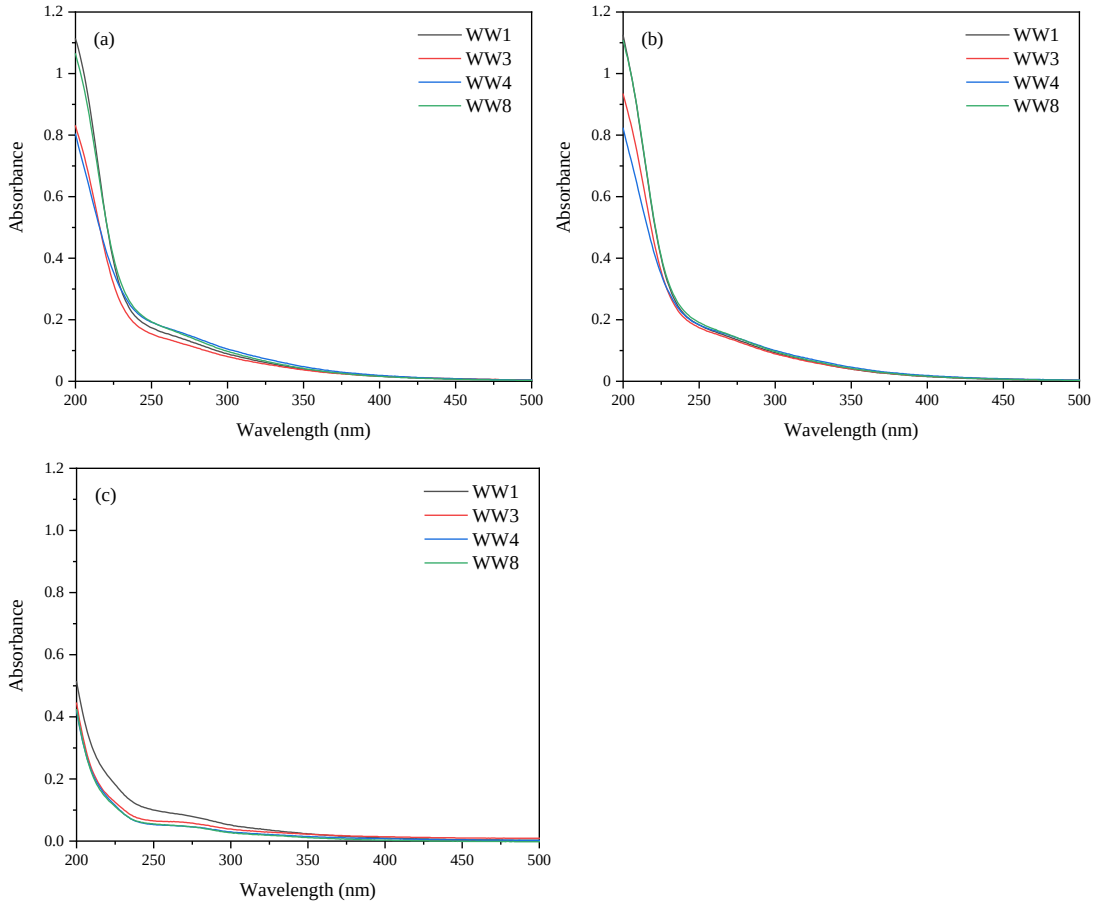

Fig. S4 The UV-Vis spectrum of (a) SE_{DOM}; (b) AE_{DOM}; (c) DS_{DOM} from four WWTPs (DOM: 5 mg C/L).

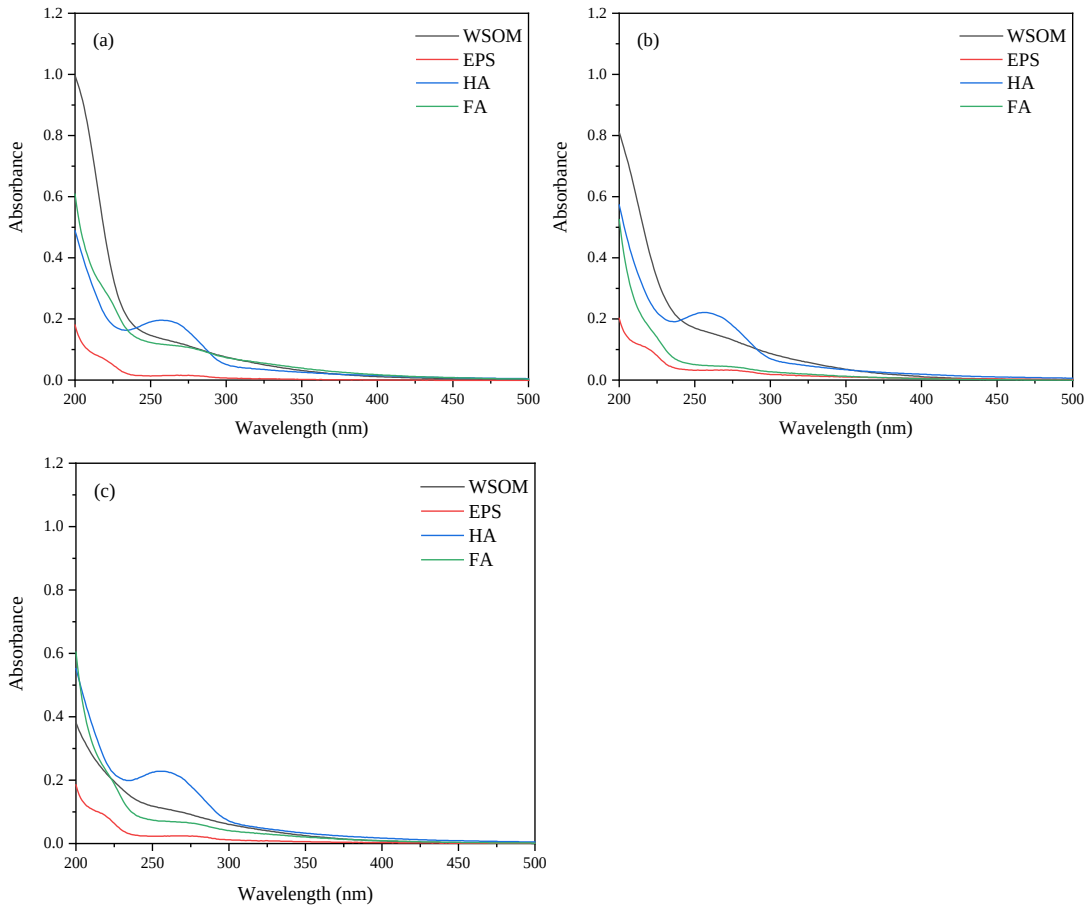

Fig. S5 The UV-Vis spectrum of DOM solutions from A^2/O process of WW8 (DOM: 5 mg C/L). (a) oxic tank; (b) anoxic tank; (c) anaerobic tank.

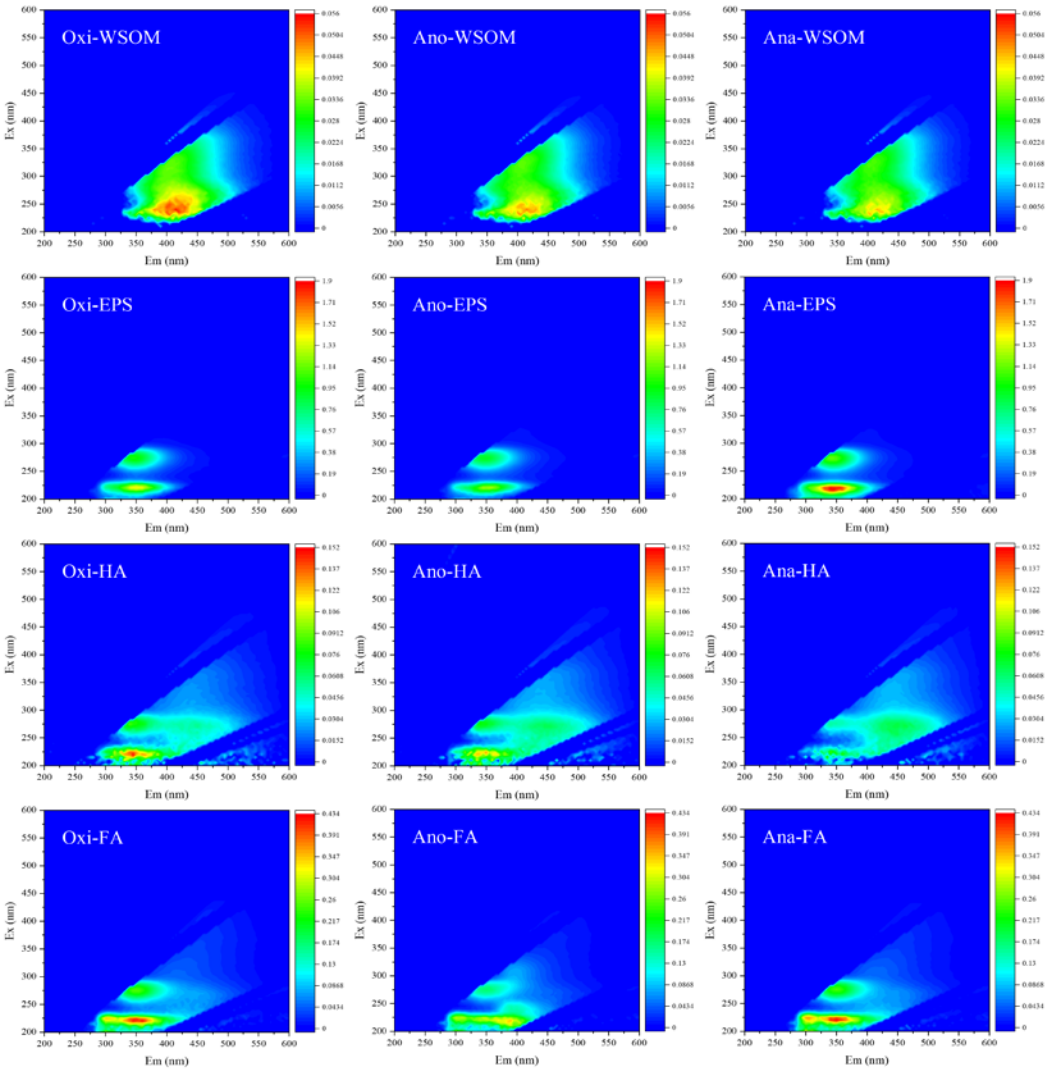

Fig. S6 Fluorescence spectrum of the WSOM, EPS, HA, and FA from A^2/O process.

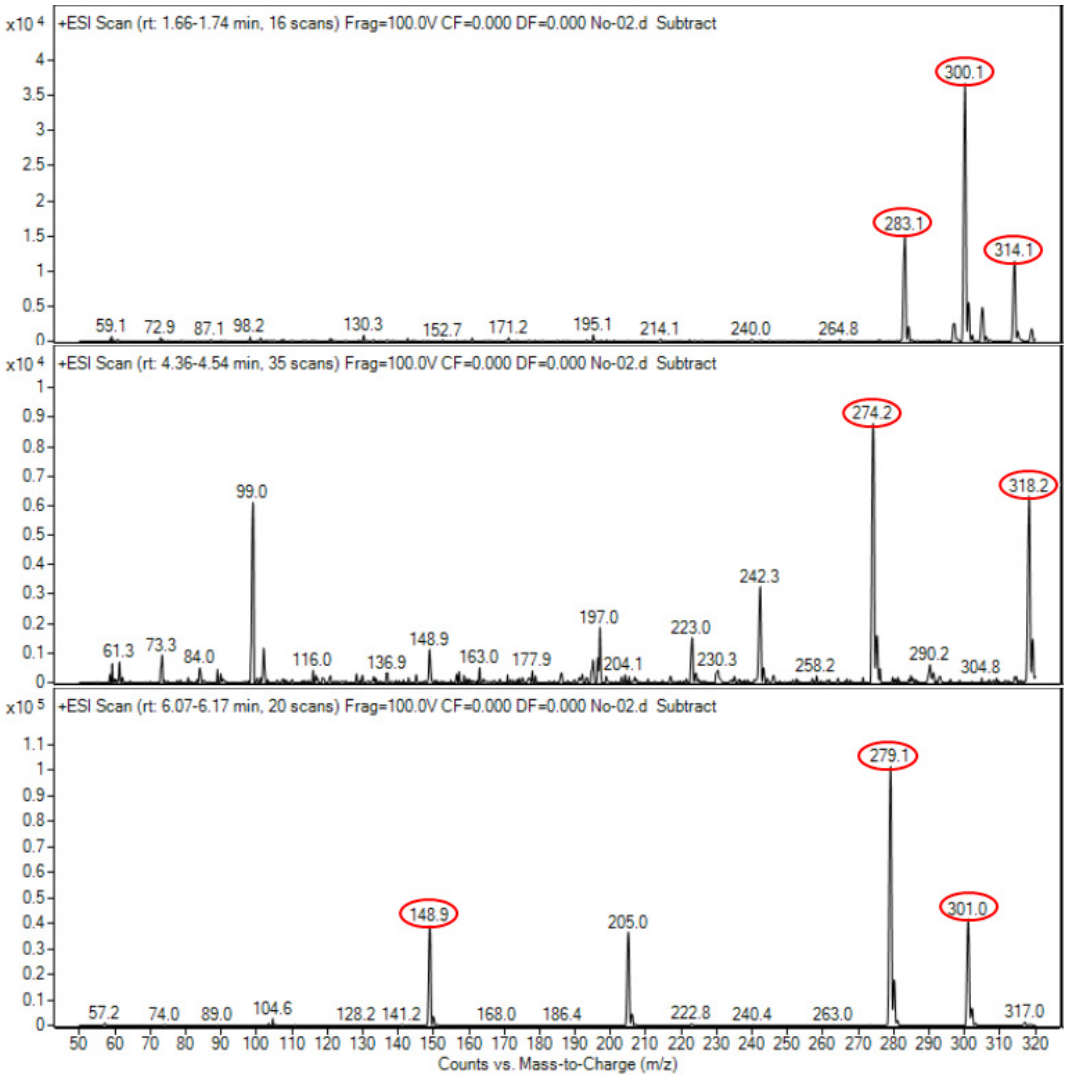

Fig. S7 Photodegradation products analyze of EE2 through LC-MS.