Electronic Supplementary Material (ESI) for Dalton Transactions.

Clay-catalyzed ozonation of Endocrine-disrupting compounds in solvent-free media - To better understand soil catalytic capacity

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Table S1. Physicochemical properties of 17α-ethinylestradiol (EE2)

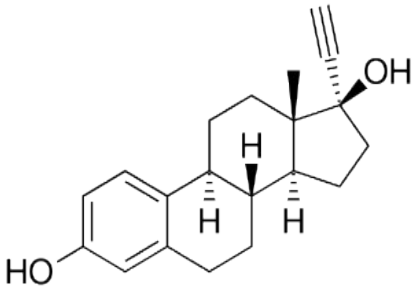
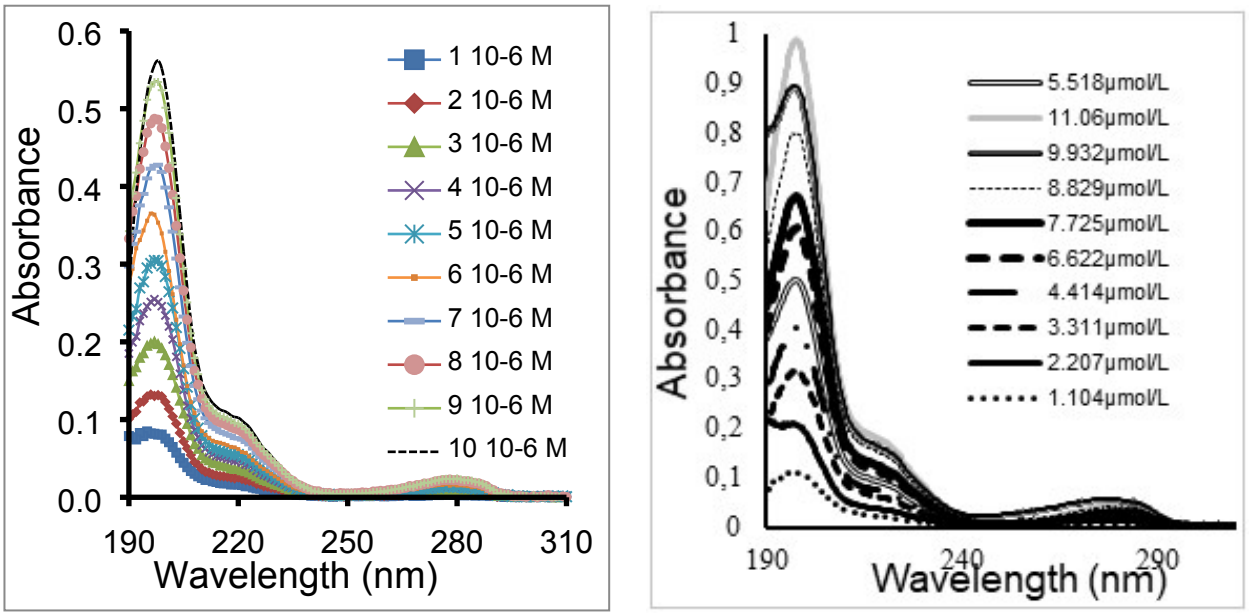
Molecular formula	
Molecular structure	$C_{20}H_{24}O_2$
Molecular weight (g/mol)	296.40
Water solubility (mg/L) at 20 °C	4.8
pKa	10.46 - 10.70
Log k_{ow}	4.15
λmax (nm)	198, 220, 280 nm

Table S2. Gradient used in LC-ToF-MS chromatographic analysis

mobile-phase	Gradient	
	Time (min)	B (%)
A : H_2O + 0,1 % formic acid B: ACN + 0,1 % formic acid	1.0	3
	6.0	85
	10.0	95
	11.0	95
	11.1	3
	15.0	3

Calibration of EE2 absorbances in the UV-Vis spectra



a ***b***

Fig. S1. UV-vis spectra of EE2 at different concentration in distilled water at intrinsic pH 5.28 (***a***) and in 99.998-0.001 water- ethanol mixture at pH 4.02 (***b***). Quartz cell = 1 cm. T= 22°C.

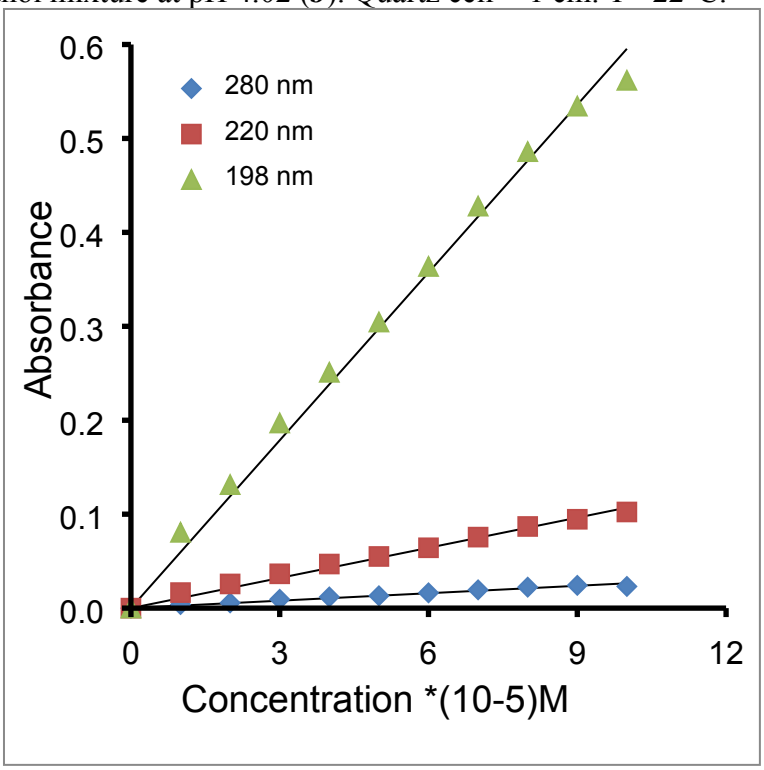


Fig. S2. Calibration curves for EE2 in distilled water. T = 22 °C. pH = 5.28. Quartz cell = 1 cm.

Table S3. Molar extinction coefficients (ε) for the three UV-Vis bands of EE2.

λ_{max} (nm)	aqueous- ethanol solution			aqueous solution		
	198	220	280	198	220	280
ε ($M^{-1}.cm^{-1}$)	88100	16800	4600	5960	1070	260
R^2	0.999	0.997	0.988	0.993	0.989	0.972
[EE2] ($\mu mol.L^{-1}$)	0 – 11.06	0 – 11.06	0.5 – 5.5	0 – 10	0 – 10	0 – 10

LC-ToF-MS analysis of the evolution in time of the EE2 ozonation in aqueous solution

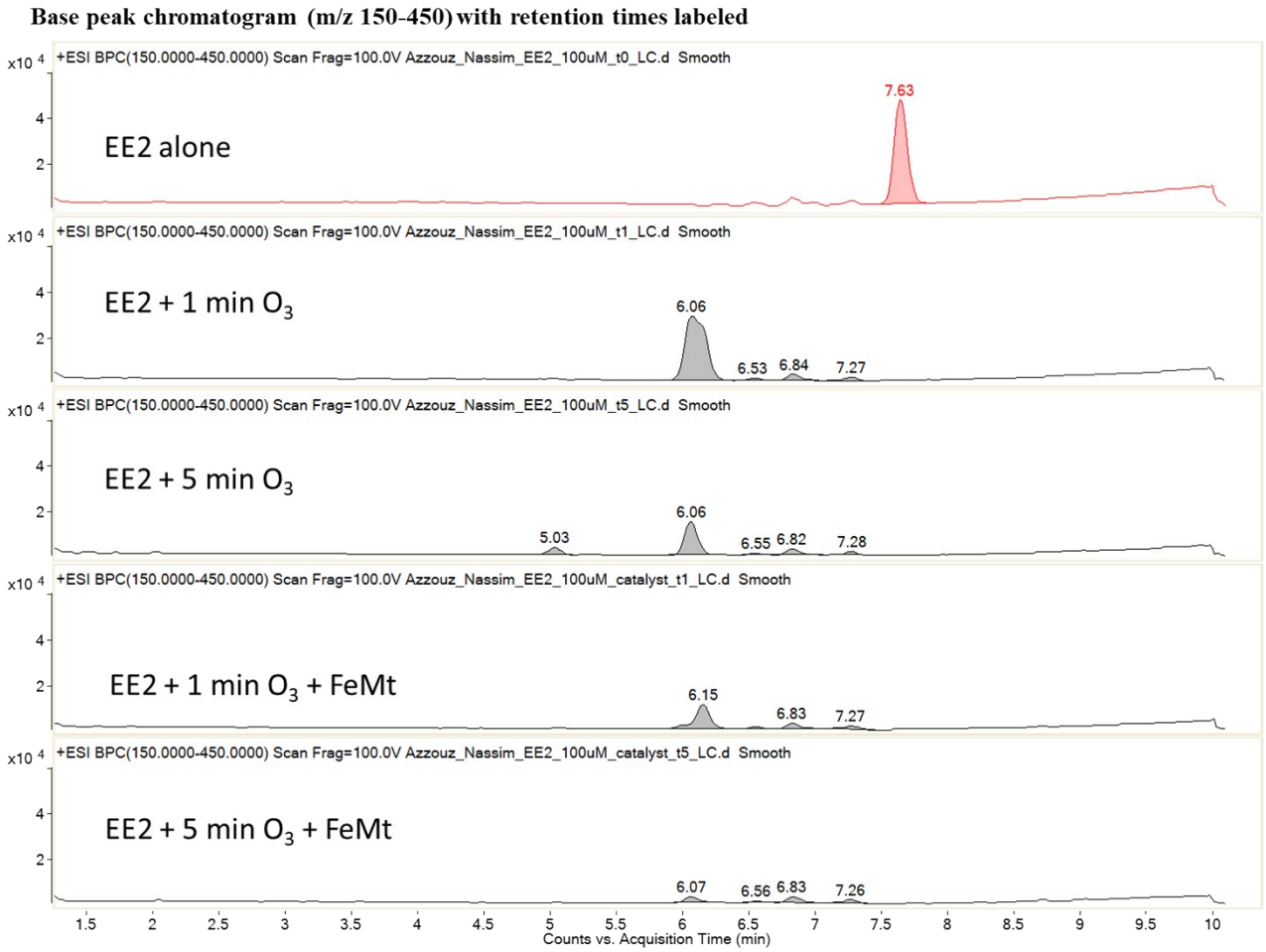
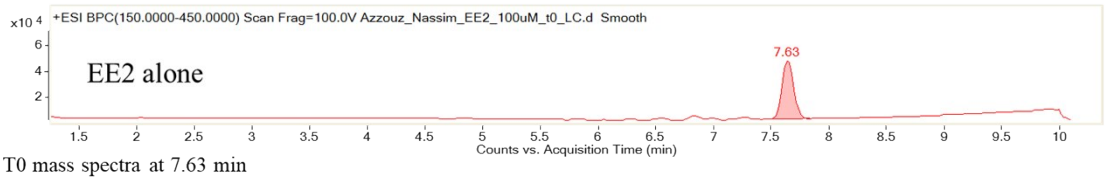


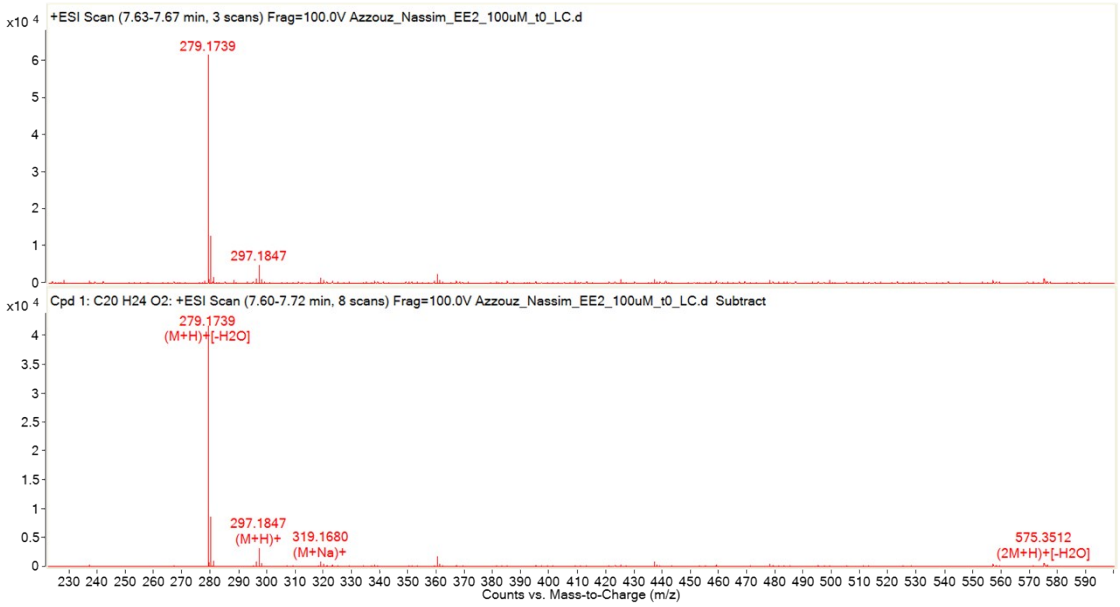
Fig. S3. Effect of Fe(II)Mt addition on EE2 degradation as evaluated by LC-ToF-MS analysis of the ozonation mixture in water. Initial EE2 concentration = 10^{-5} M, Fe(II)Mt concentration: 2 g L^{-1}, Ozone dose: 600 mg h^{-1} at 22 °C

Intermediate identification by LC-ToF-MS analysis of the ozonation mixture in water

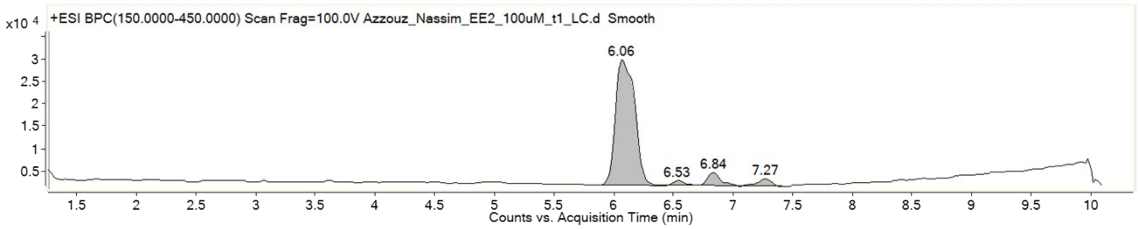
T0 Base peak chromatogram (*m/z* 150-450) with retention times labeled



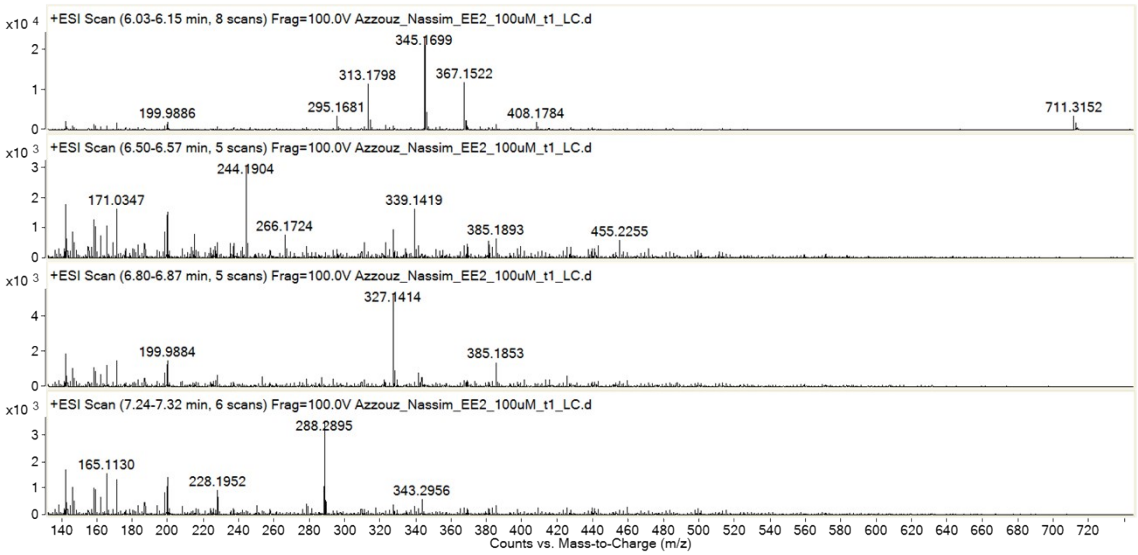
T0 mass spectra at 7.63 min



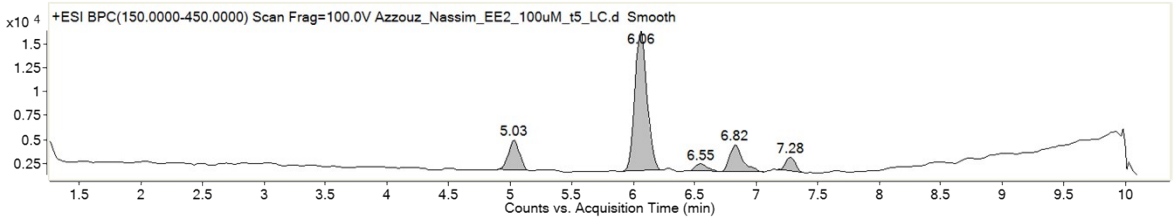
EE2 + 1 min O_3 base peak chromatogram (*m/z* 150-450) with retention times labeled



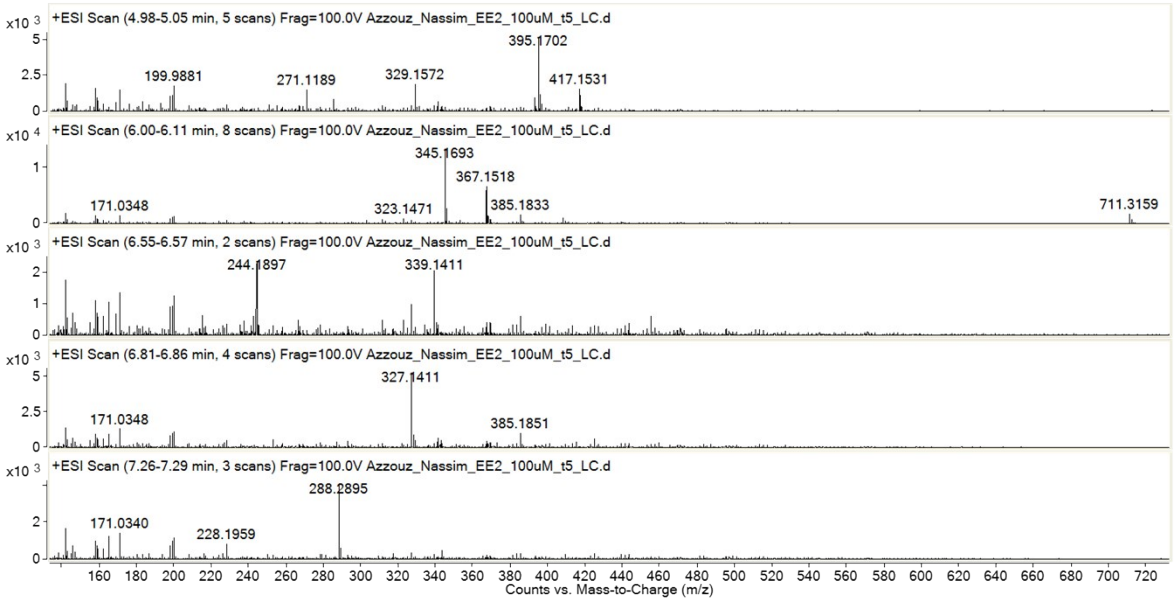
t1 mass spectra at 6.06, 6.53, 6.84, 7.27 min



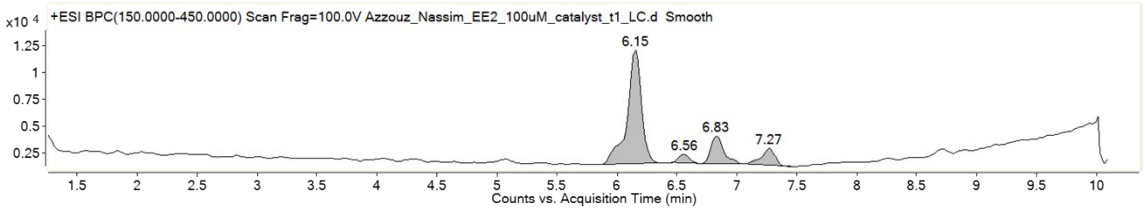
EE2 + 5 min O_3 base peak chromatogram (*m/z* 150-450) with retention times labeled



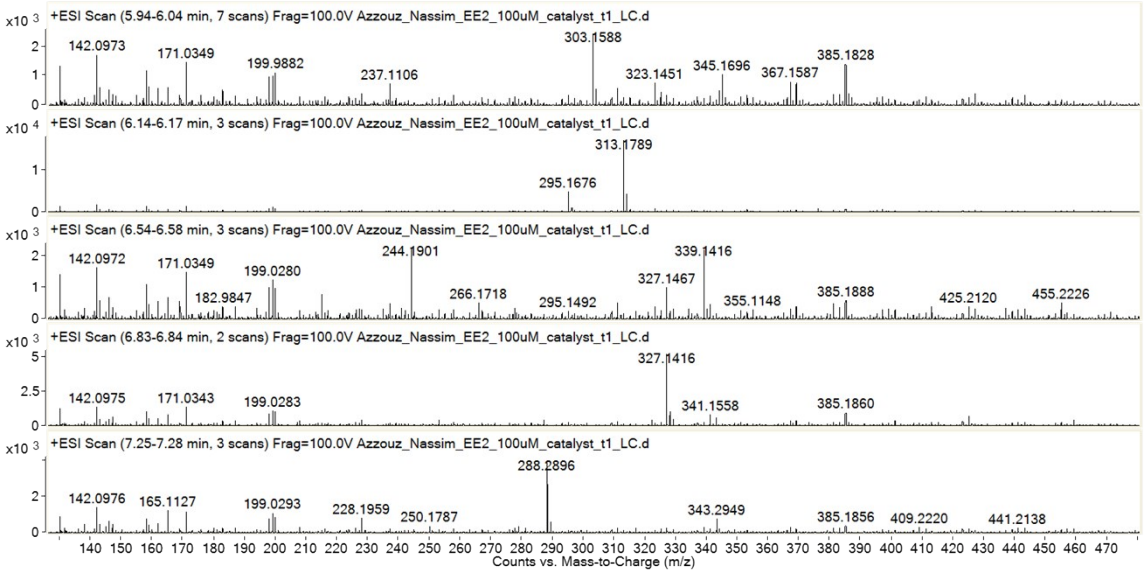
t5 mass spectra at 6.06, 6.53, 6.84, 7.27 min



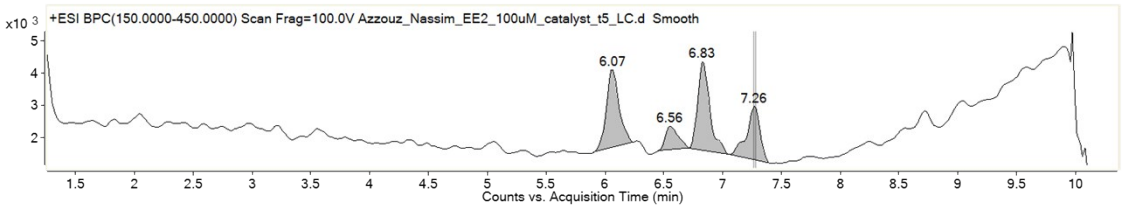
EE2 + 1 min O_3 + FeMt base peak chromatogram (*m/z* 150-450) with retention times labeled



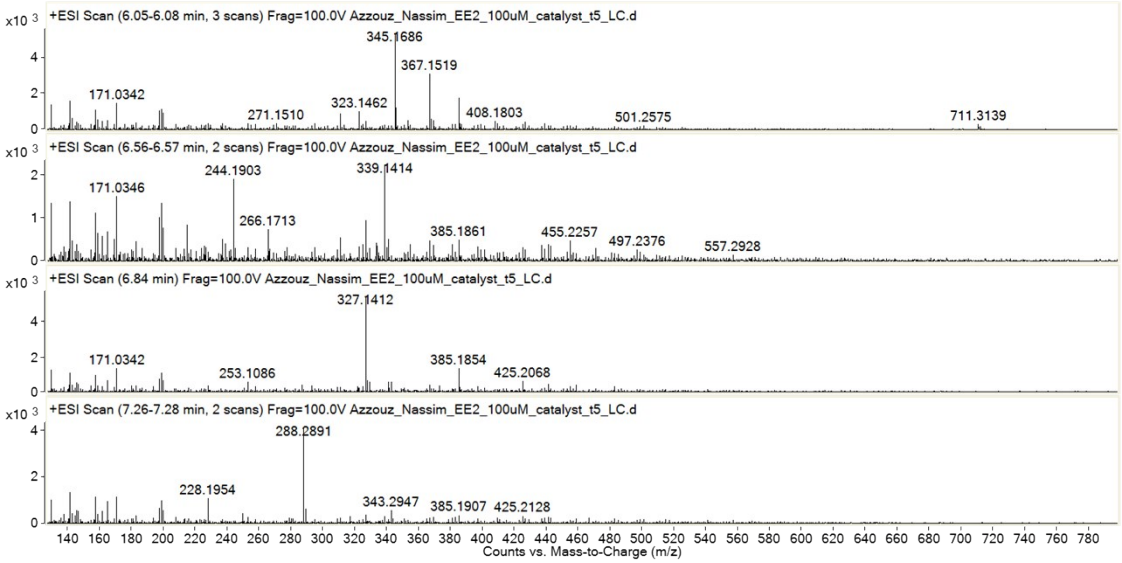
t1 + c mass spectra at 5.95, 6.15, 6.56, 6.83, 7.27 min



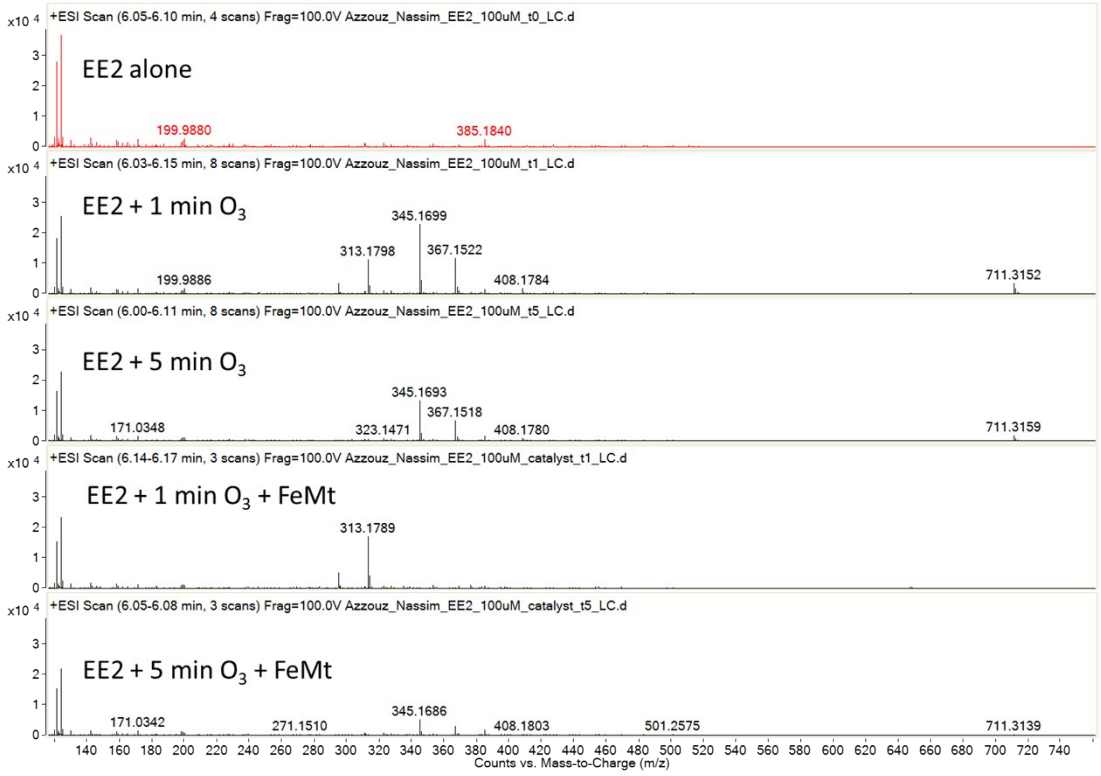
EE2 + 5 min O_3 + FeMt base peak chromatogram (*m/z* 150-450) with retention times labeled



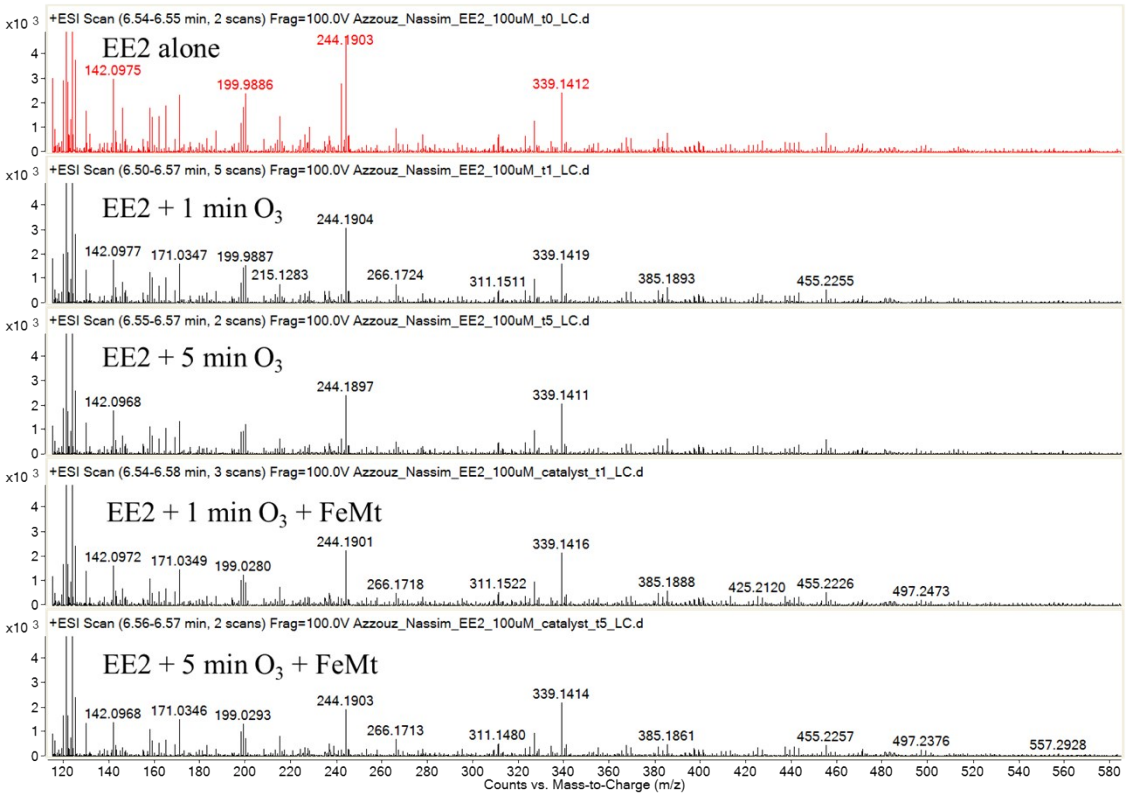
mass spectra at 6.06, 6.56, 6.83, 7.26 min



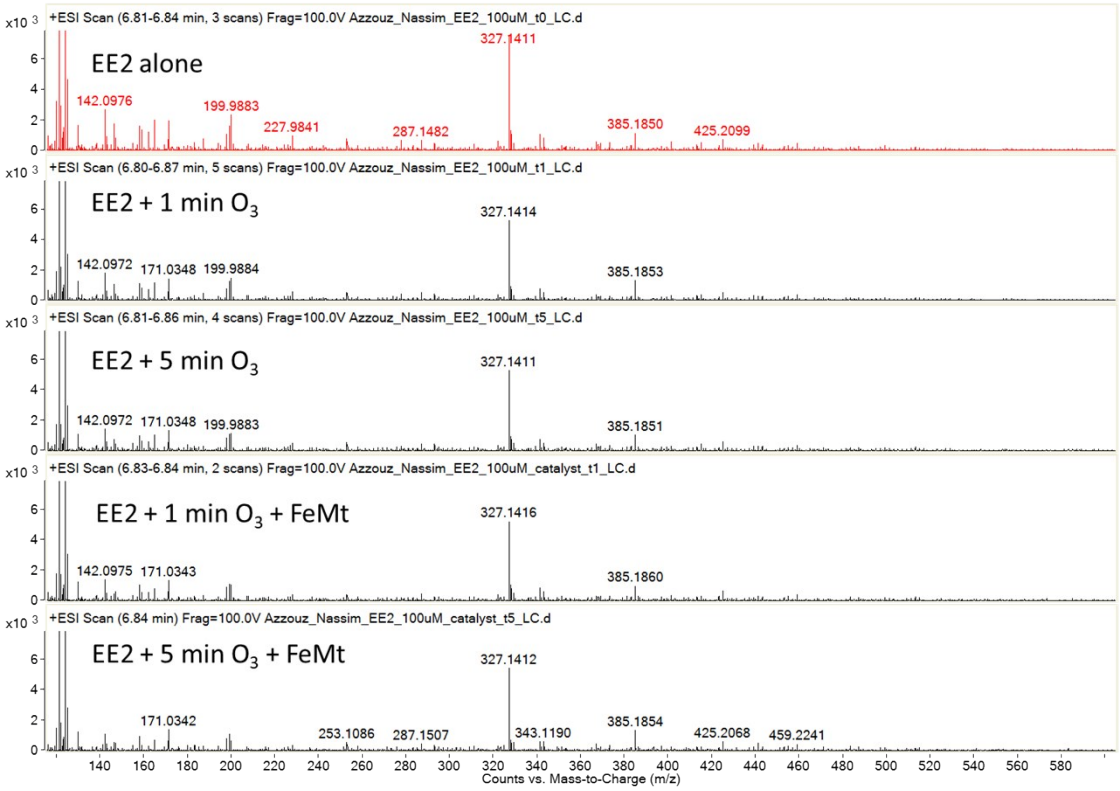
Comparison of mass spectra at 6.05 min



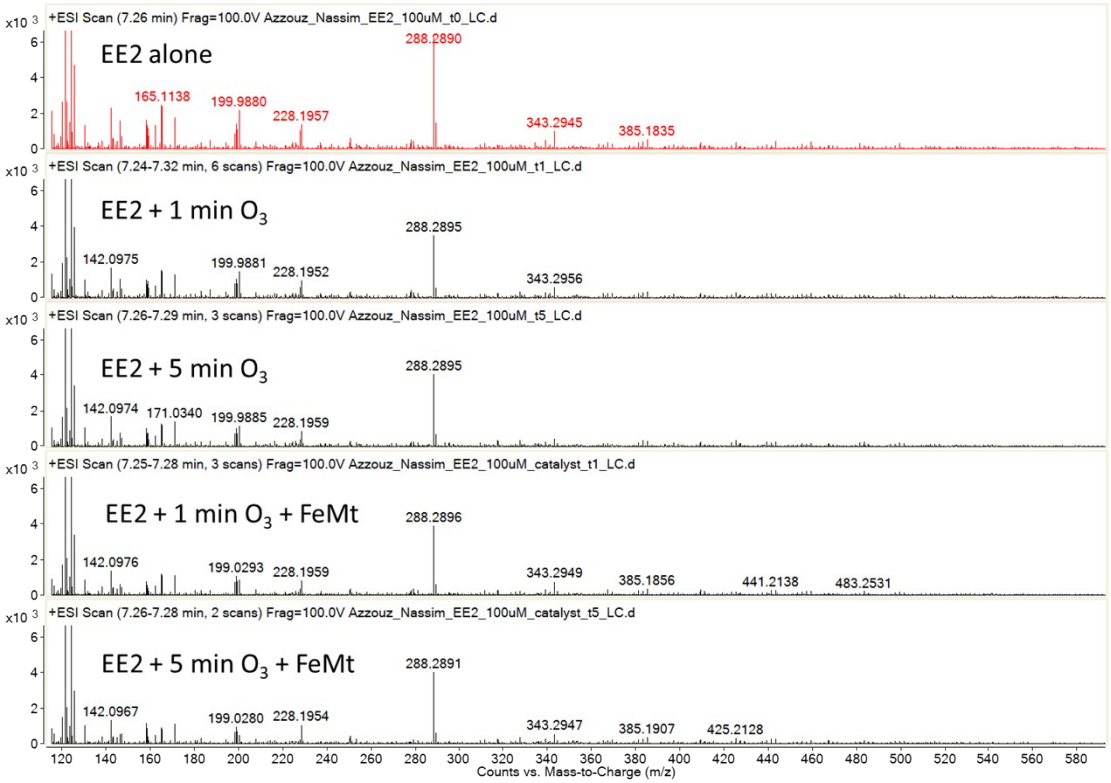
Comparison of mass spectra at 6.5 min



Comparison of mass spectra at 6.8 min



Comparison of mass spectra at 7.26 min



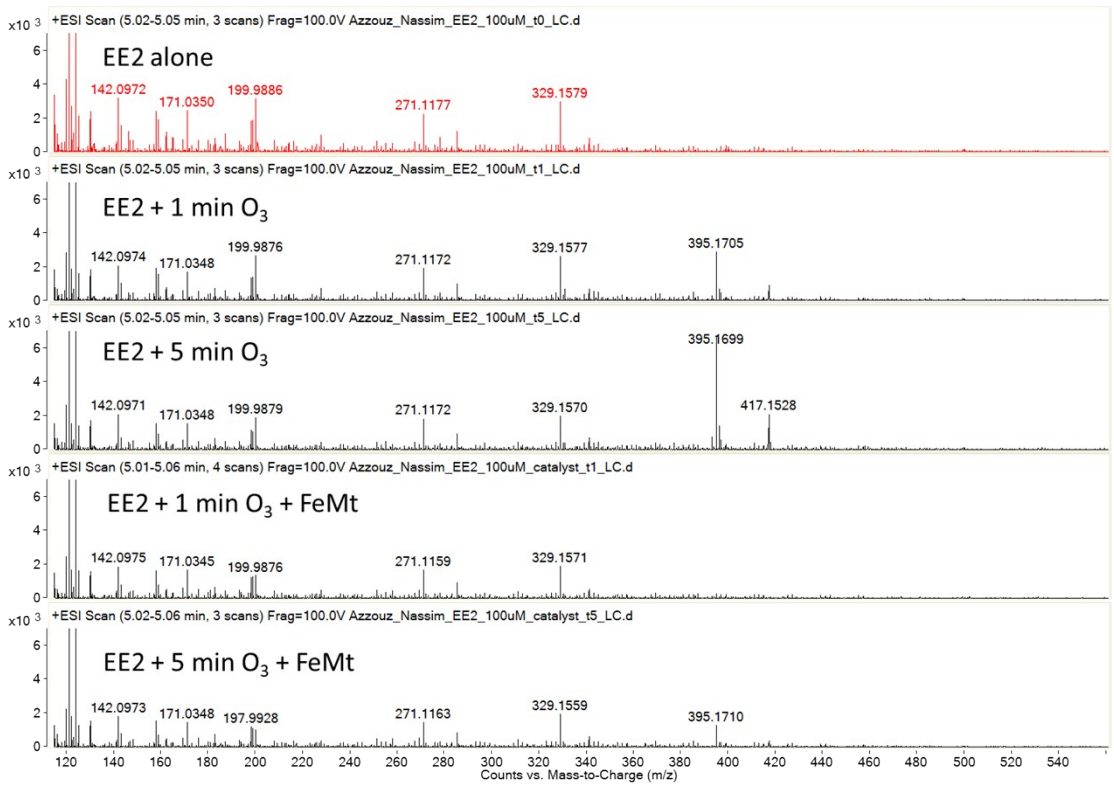
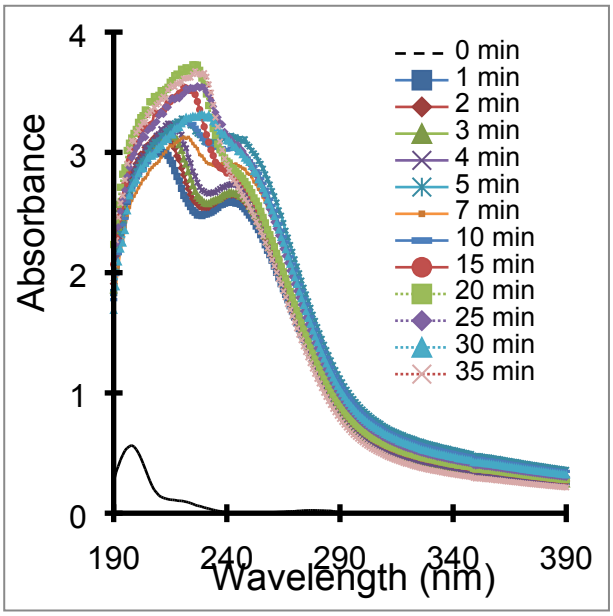
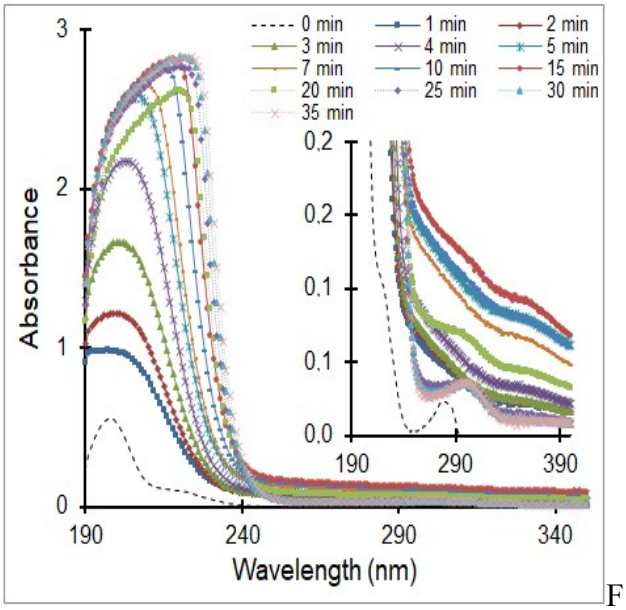


Fig. S4. LC-ToF-MS diagram of EE2 ozonation mixture after 1 and 5 min ozonation in the absence (a) and presence of Fe(II)Mt (b) in aqueous solution. Initial EE2 concentration = 10^{-5} M, Fe(II)Mt concentration: 2 g L^{-1}, Ozone dose: 600 mg h^{-1} at 22 °C.

Effect of the exchangeable cation during EE2 ozonation in water

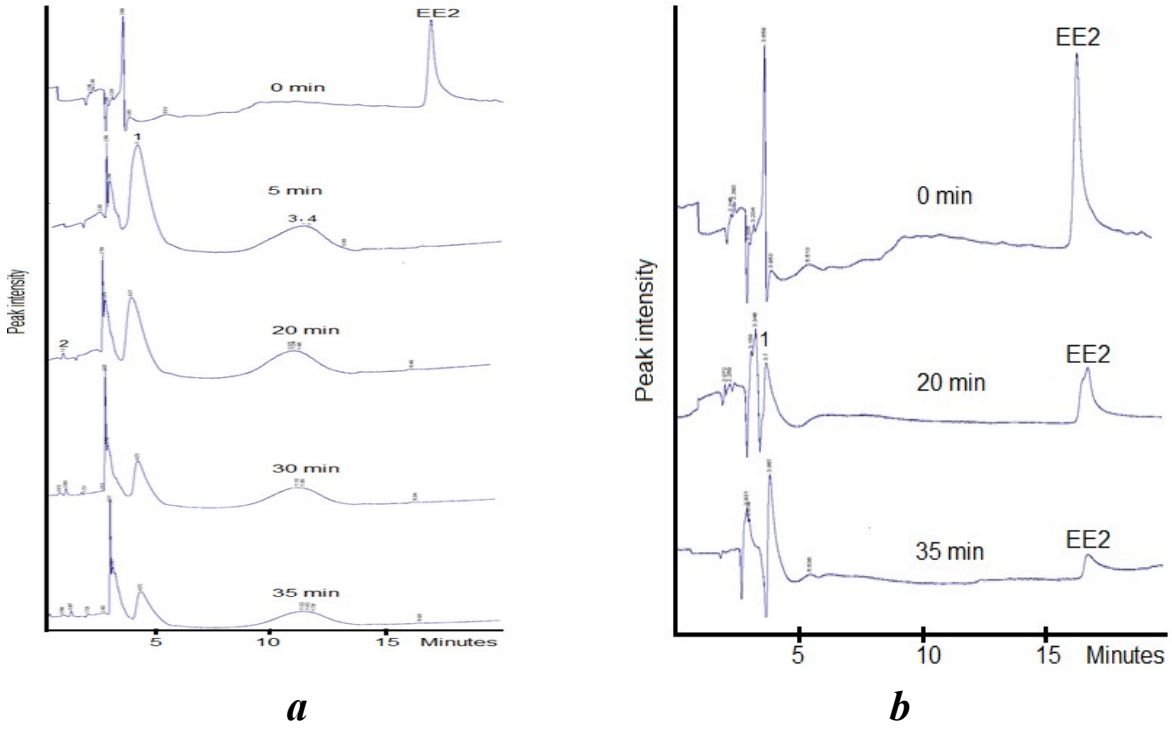


NaMt



Fe(II)Mt

Fig. S5. UV-vis spectra of EE2 after catalytic ozonation in aqueous solutions. T = 22 °C. pH = intrinsic. Quartz cell = 1 cm.O_3 throughput: 600 mg.h^{-1}.Sample volume = 20 mL. Initial concentration: 10^{-5} M. Catalyst amount = 40 mg.



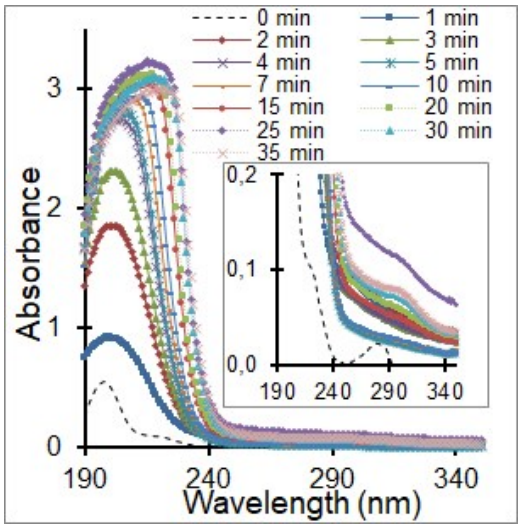
a ***b***

Fig. S6. HPLC diagrams of the ozonation mixture in the presence of NaMt **(a)** and Fe(II)Mt **(b)** in distilled water as detected by UV detector at wavelength of 280 nm. T = 22 °C. pH = intrinsic. Concentration: 10^{-5} M.

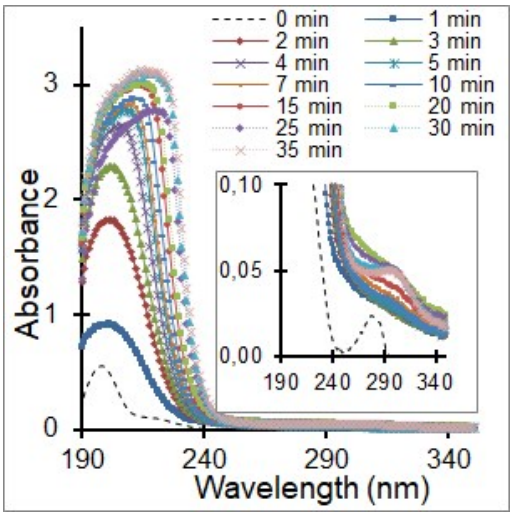
Table S4. Retention time and area peak after 35 min of EE2 ozonation.

Catalyst	None		NaMt		Fe(II)Mt	
HPLC-UV peak	Retention time (min)	Peak area	Retention time (min)	Peak area	Retention time (min)	Peak area
EE2	16.69	1571	16.42	1062	16.15	7934
Intermediate 1	3.86	77373	11.74	45997	2.93	18196
Intermediate 2	3.51	25660	11.47	17592	3.02	9402
Intermediate 3	3.41	12689	11.22	102030	3.87	64836
Intermediate 4	3.32	16292	4.07	100272	5.54	2074
Intermediate 5	2.81	12043	2.83	86027	-	-
Intermediate 6	-	-	2.71	33-92	-	-
Intermediate 7	-	-	2.43	4737	-	-
Intermediate 8	-	-	1.73	1284	-	-
Intermediate 9	-	-	-.99	2856	-	-
Intermediate 10	-	-	-.6-	1129	-	-

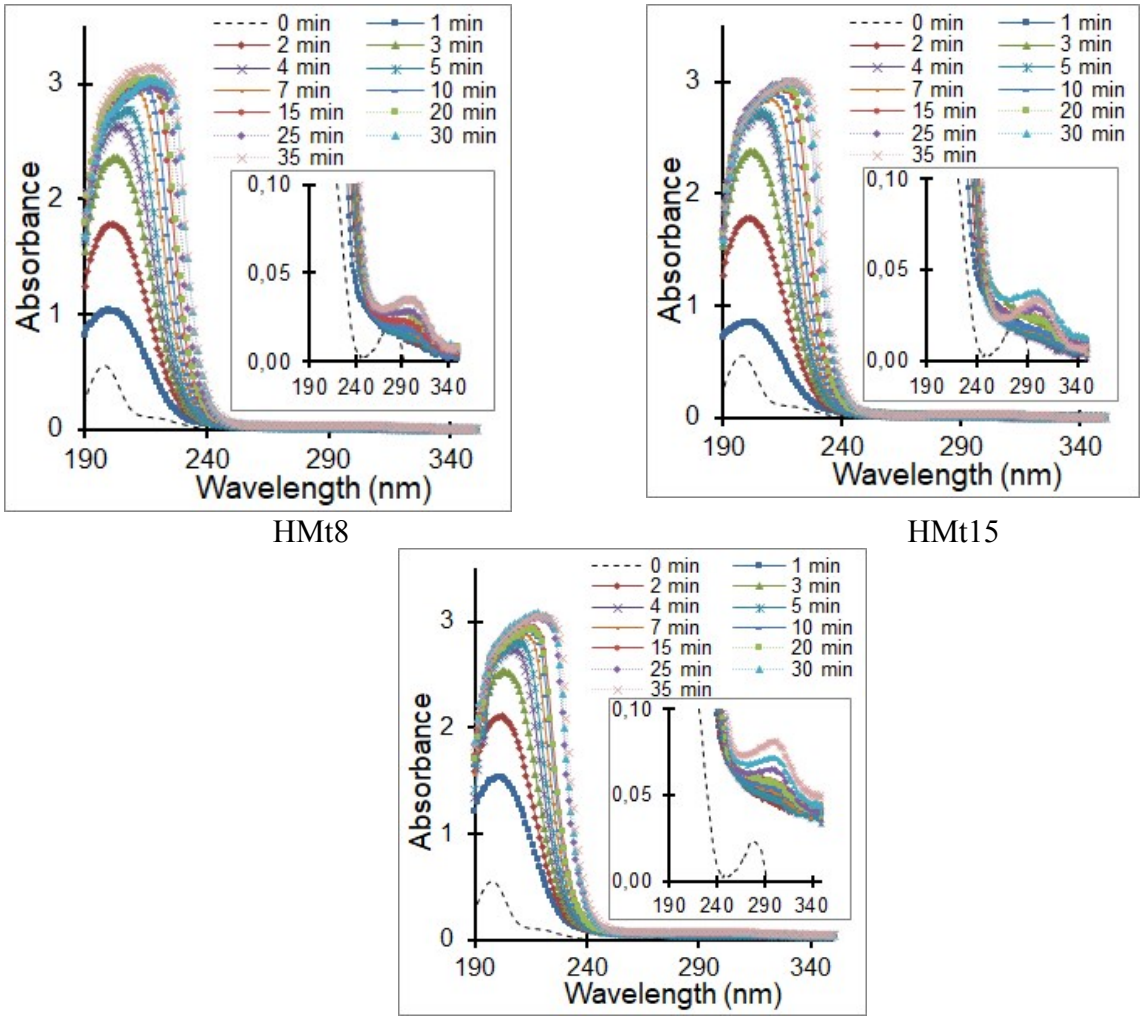
Catalytic activity of acid-activated bentonites



HMt1



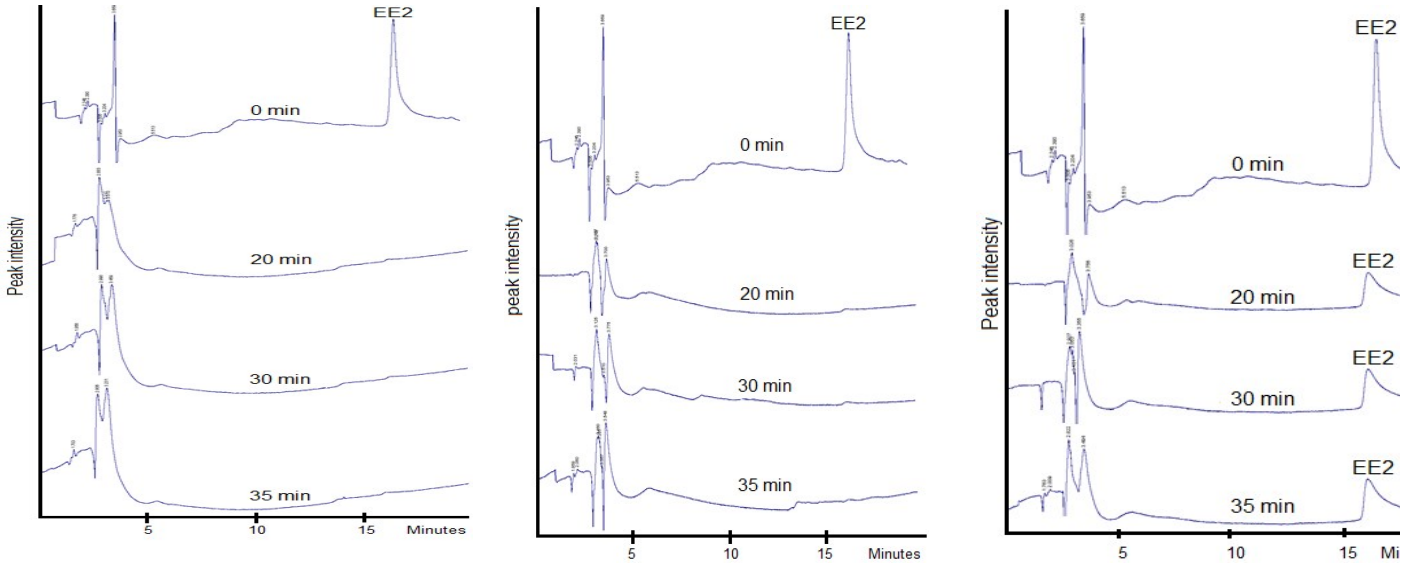
HMt4



HMt8 HMt15

HMt24

Fig. S7. UV-vis spectra of the ozonation mixture in the presence of acid-activated bentonites in aqueous EE2 solution. T = 22 °C. Quartz cell = 1 cm.O_3 throughput: 6-- mg.h^{-1}.Sample volume = 2- mL. Initial concentration: 1-$^{-5}$ M. Catalyst amount = 4- mg and intrinsic initial pH.



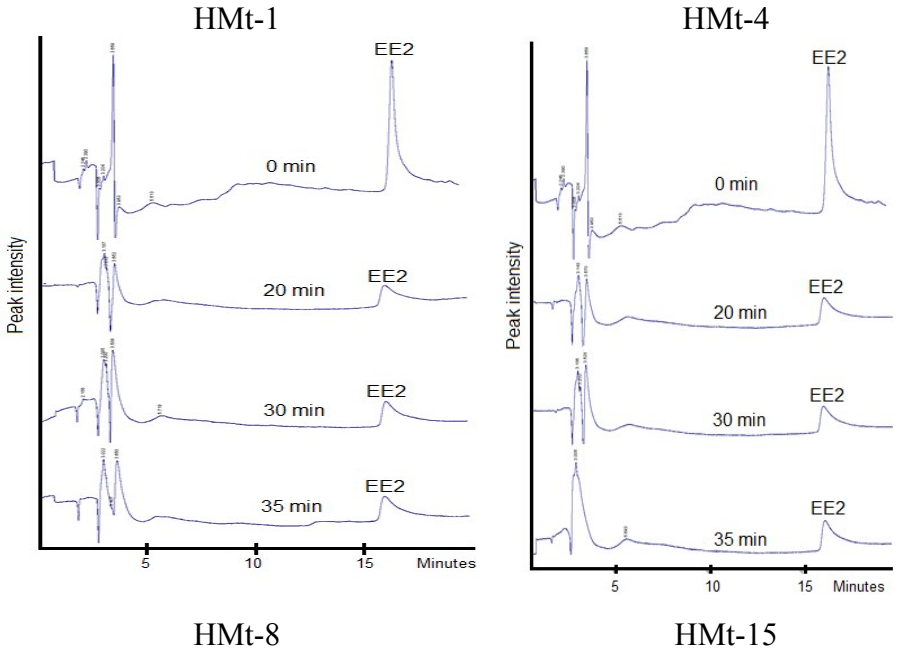


Fig. S8. HPLC-UV (28- nm) chromatograms of the initial solution of EE2 and of aliquots taken after different times of ozonation in the presence of HMt catalyst.