From batch system toward continuous UV/PS based AOP reactor: The case of Tramadol effluent

degradation

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Supporting Information

12 Pages, 3 Texts, 13 Figures, 4 Tables

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Text S1

**2.2.1 Batch UVC reactor: experimental setup**

The bench scale experimental setup was constructed using elements of a commercial UVC water disinfection apparatus: a low-pressure mercury lamp (LPHgL) (Philips TUV 11W G11 T5, Poland) and its corresponding quartz insert tube. The original stainless-steel casing was replaced with a 400 mL borosilicate reactor, which allowed easier handling and sampling and better temperature control. The reactors were placed in a temperature-controlled water bath at 20°C (PolyScience MM7 chiller). The UVC intensity was 6.25 mW cm^{-2} at a distance of 3 cm, measured using a radiometer (Model UVC-254 Lutron; Taipei, Taiwan). The lamps were turned on 30 min before starting the experiment to allow stabilized flux to obtain consistent results with such commercial tools. All experiments were performed in duplicates.

All solutions used in the degradation experiments were prepared daily using deionized water. The total volume in each reactor was 350 mL. The appropriate volumes of tramadol (TRA)stock (100 mg L^{-1}) and water are added to the reactor in the water bath before adding the appropriate volume from the PS stock (200 mM). The reaction was initiated by inserting the preheated UV lamp into the quartz insert. Two control samples were obtained before and after PS addition (labeled t = -2 and t = -1, respectively). A sample at t = 0 min was obtained just after the initiation of the degradation process. Thereafter, a 2 mL sample was obtained and immediately quenched in an ice bath every 2 min. Simulated effluent samples were filtered using a 0.45 µm PTFE filter disc before analysis.

Text S2

2.2.1 Batch UVC reactor: Iodide/iodate actinometry

Iodine/iodate chemical actinometry was performed according to the standard IUPAC method to determine the absorbed photon flux in the reactor. For this purpose, a solution of 0.6 M Iodine and 0.1 M iodate (buffered at pH = 9.25) was prepared. A 0.01 M borate buffer was utilized. This solution absorbs photons and generates triiodide (I_3^-) ions through the oxidation of iodide, according to the reaction below:

$$8\ KI\ +\ KIO_3\ +\ 3\ H2O\ +\ h\nu\ \rightarrow\ 3\ I_3^-\ +\ 6\ OH^-\ +\ 9\ K^+$$
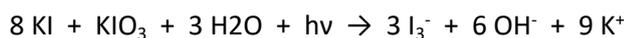
Obtaining the quantum yield of this system allows the determination of the absorbed photon flux in Einstein s^{-1}. The absorbance values of this solution at 300 nm and 352 were recorded to quantify the iodide (I^-) and I_3^- ions, respectively. The molar extinction coefficients of these two ions are known; therefore, obtaining their concentration is possible using the Beer-Lambert law:

$$A = \varepsilon l c$$

where A is the absorbance of the solution at a certain wavelength in a.u., ε is the molar absorption coefficient of the absorbent of interest at the same wavelength in M^{-1}cm^{-1}, l is the cell path length (1 cm in our case), and c is the concentration of the absorbent in M.

Table S1 shows the absorbance values of the actinometric solution initially (unirradiated) and after 6 min of irradiation (total TRA degradation time). The sample obtained after 6 min was diluted 20 folds using the initial solution because the increase in I_3^- caused an increased absorbance at 352 nm, which exceeded the spectrophotometer limits. This dilution was considered when calculating I_3^- in the original sample.

The standard IUPAC method uses a formula to calculate the quantum yield, adjusted to temperature and [I-]. In our experiment, [I$^-$] was equal to 0.6 M, and the temperature was slightly different at 21.0°C instead of 20.7 °C:

$$\Phi = 0.75\ ([1 + 0.02\ (T - 20.7)]\ [1 + 0.23\ (C - 0.577)]$$
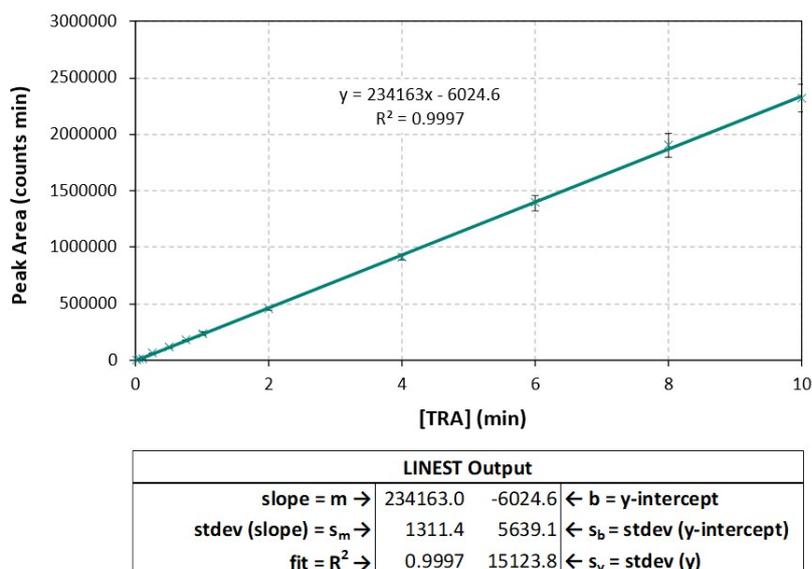
where T is the temperature in °C and C is [I$^-$] in M.

The absorbed photon flux was subsequently calculated by dividing the number of moles of I_3^- generated by the quantum yield, which was calculated to be $\Phi = 0.75$. The obtained results are shown in Table S1. The absorbed photon flux in our reactor was equal to 8.07×10^{-8} Einstein s^{-1}.

Table S1. Data used in the chemical actinometry experiment

Wavelength (nm)	Absorbance (a.u.)	
	Initial (unirradiated)	Final (after 6 min)*
352	0.0246	0.2457
300	0.5890	0.8366
ε for I_3^- at 352 nm (M^{-1}cm^{-1})		27600
ε for I^- at 300 nm (M^{-1}cm^{-1})		1.061
[I^-] in non-irradiated sample (M)		0.555
[I_3^-] in diluted sample (M)		8.902E-06
[I_3^-] in original sample (M)		**1.780E-04**
Number of moles of I_3^- (mol)		6.232E-05
Quantum Yield		0.75
Absorbed photon flux (Einsteins s^{-1})		8.07E-08
Number of photons absorbed (photons)		1.75E+19
Energy absorbed (J)		**39.18**
Power (W)		0.1088

*Note that this absorbance is for a solution diluted 20 folds using the initial actinometric solution

| LINEST Output			
slope = m →	234163.0	-6024.6	← b = y-intercept
stdev (slope) = s_m →	1311.4	5639.1	← s_b = stdev (y-intercept)
fit = R^2 →	0.9997	15123.8	← s_y = stdev (y)

Fig. S1 TRA calibration curve and LINEST output

Text S3

2.3.2 HPLC-QTOF-MS/MS

The LC method was adapted from that used in the HPLC/FLD, except for switching the aqueous eluent from 0.01 M phosphate buffer to ammonium formate (with 0.1% formic acid) due to ESI compatibility issues.

The mass spectra of TRA transformation products were acquired using HPLC coupled to quadrupole time-of-flight tandem mass spectrometry (Sciex X500R HPLC-QTOF-MS/MS, Sciex Applied Biosystems, Framingham, MA, USA). The electrospray ion source was operated in the positive ion mode under a spray voltage of 5500 V and MS collision energy set to 10 V.

The methodology adopted to determine the TPs was as follows: searching the literature for reported products by other oxidation techniques → extracting ion chromatograms based on the obtained TPs → removing the background signal → determining the mass spectra of the obtained extracted ion chromatogram (XIC) peaks → developing a processing method to determine the mass accuracy and error in retention time of the identified TPs.
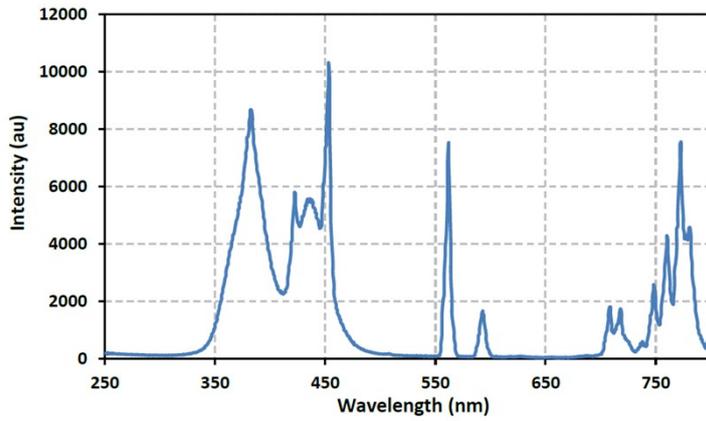
Fig. S2. Emission spectrum of the UVA lamps used
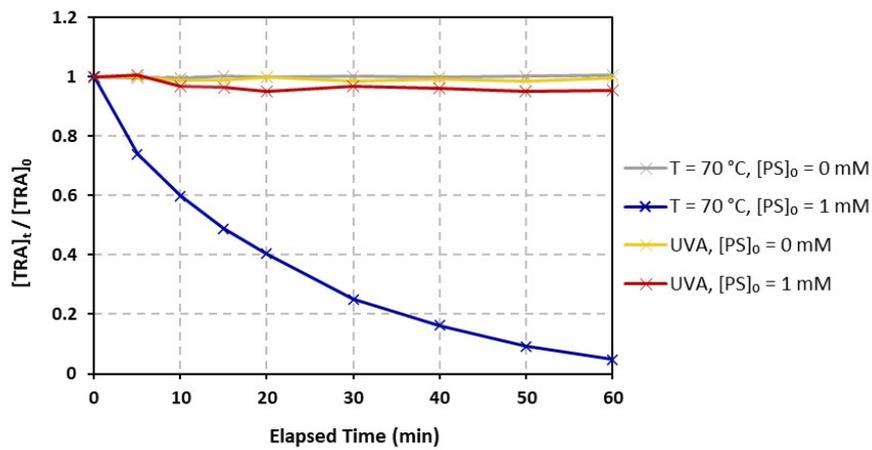
Fig. S3 The degradation of TRA as a function of reaction time (min) under thermal and UVA PS activation conditions
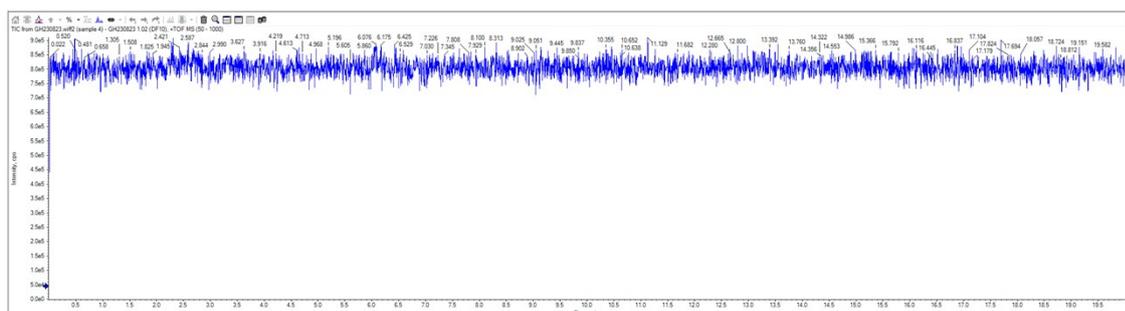
$[TRA]_0 = 10$ mg L^{-1}
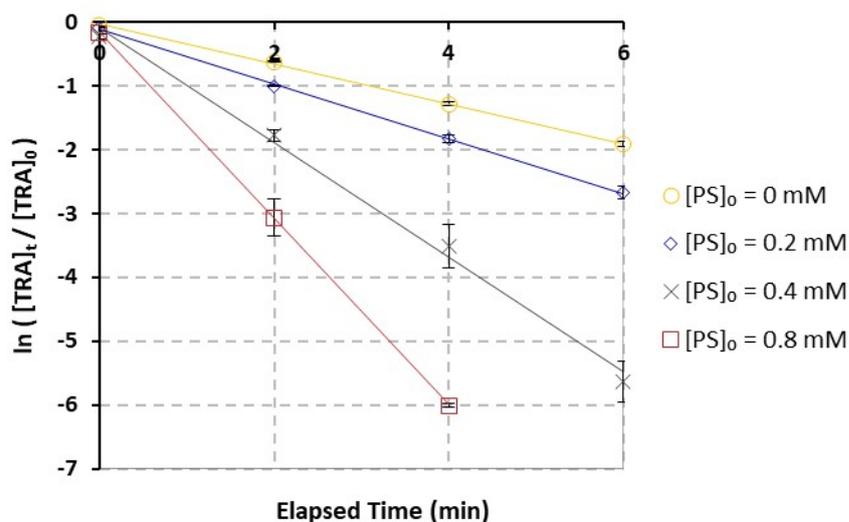
Fig. S4 Plot of ln $\frac{[TRA]}{[TRA]_0}$ as a function of elapsed reaction time
The slope of each line is the k_{obs} obtained at the corresponding $[PS]_0$

**Table S2.** Regression coefficients and k_{obs} (slope) of the curves in Fi

[PS] (mM)	R^2	k_{obs} (min^{-1})
0	0.999	0.31
0.2	0.999	0.43
0.4	0.995	0.90
0.8	0.999	1.46

Table S3. The proposed transformation products from the oxidation with UVC/PS and their corresponding m/z and molecular formulas system.

Compound ID	Mass/charge ratio (m/z)	Molecular Formula
Tramadol (TRA)	264.1958	$C_{16}H_{26}NO_2$
TP280a (N-OXID)	280.1907	$C_{16}H_{26}NO3$
TP280b	280.1907	$C_{16}H_{26}NO_3$
TP250a (N-DES)	250.1802	$C_{15}H_{24}NO2$
TP250b (O-DES)	250.1802	$C_{15}H_{24}NO2$
TP236 (BIDES)	236.1645	$C_{14}H_{21}NO_2$
TP278	278.1751	$C_{16}H_{25}NO_3$
TP296	296.1865	$C_{16}H_{26}NO_4$
TP312	312.1816	$C_{16}H_{26}NO_5$

Fig. S5 TIC of the sample taken at 2 min from the UVC/PS system ($[TRA]_0$ =10 mg L^{-1}, $[PS]_0$ = 0.4 mM, and dilution factor = 10)
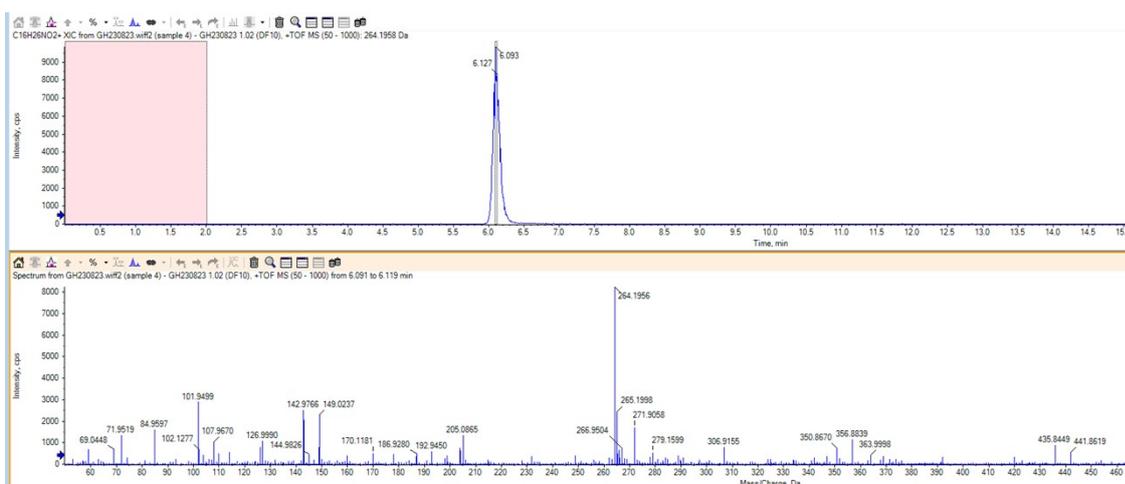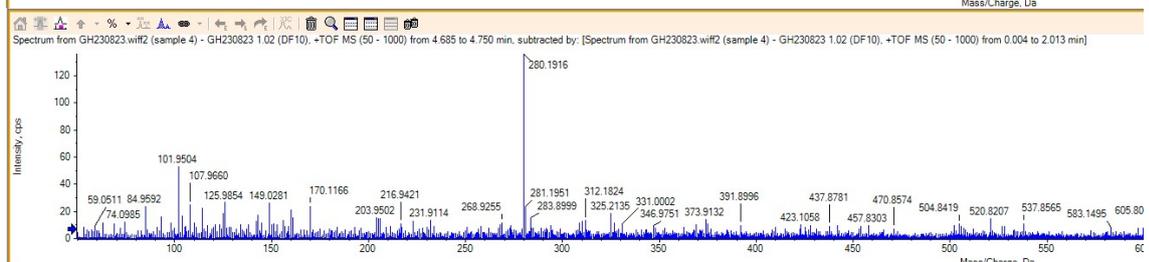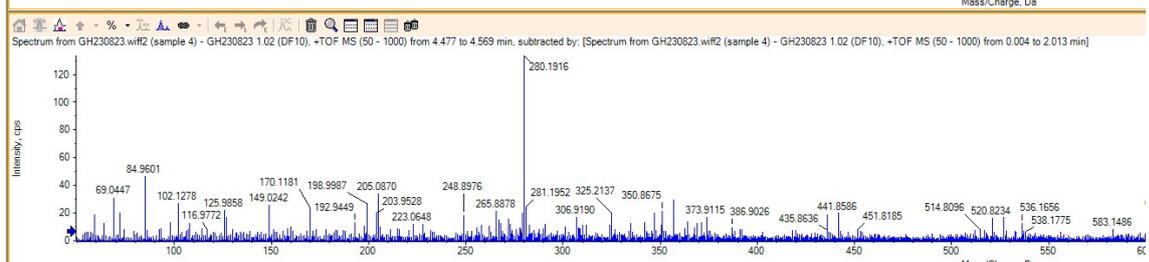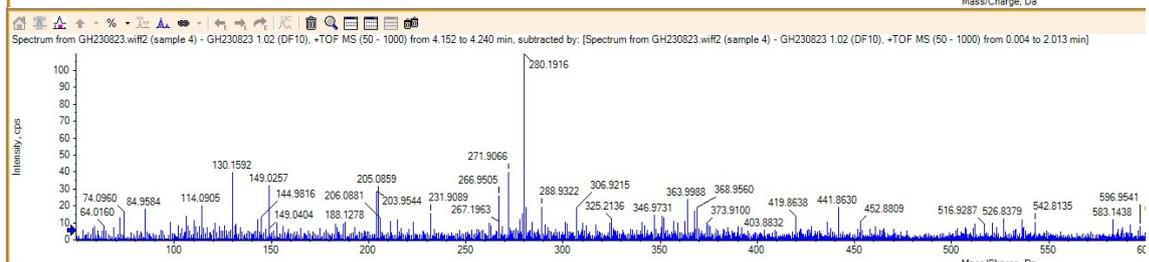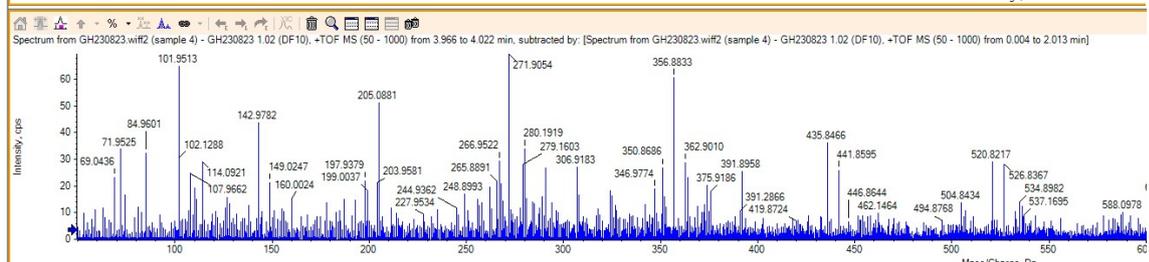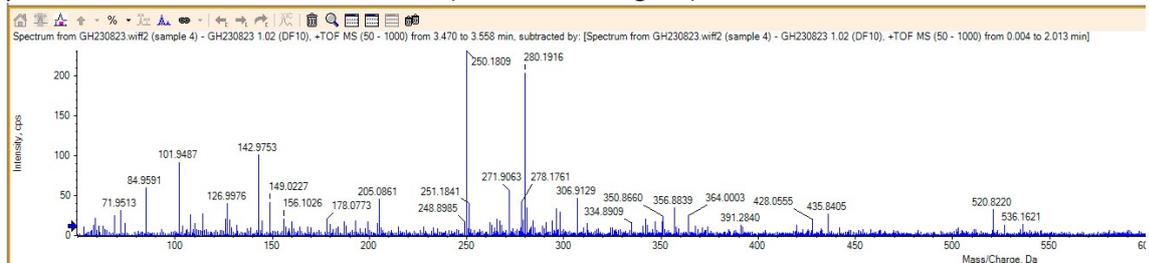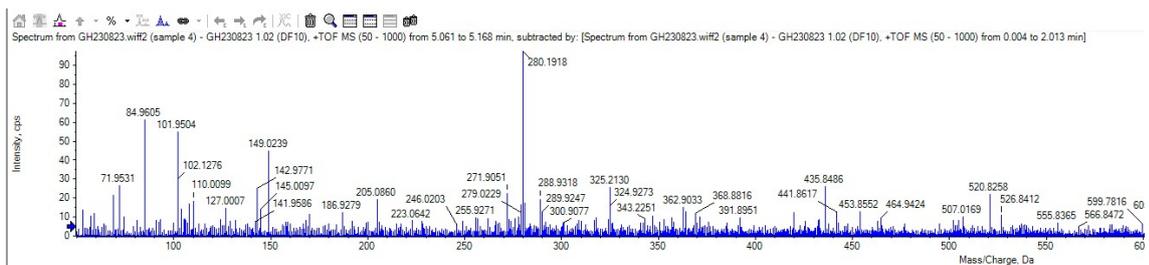

Fig. S6 The XIC for TRA ($C_{16}H_{26}NO_2$), m/z = 264.1956, width 0.01 Da, and the mass spectrum for the peak eluted at 6.093 min
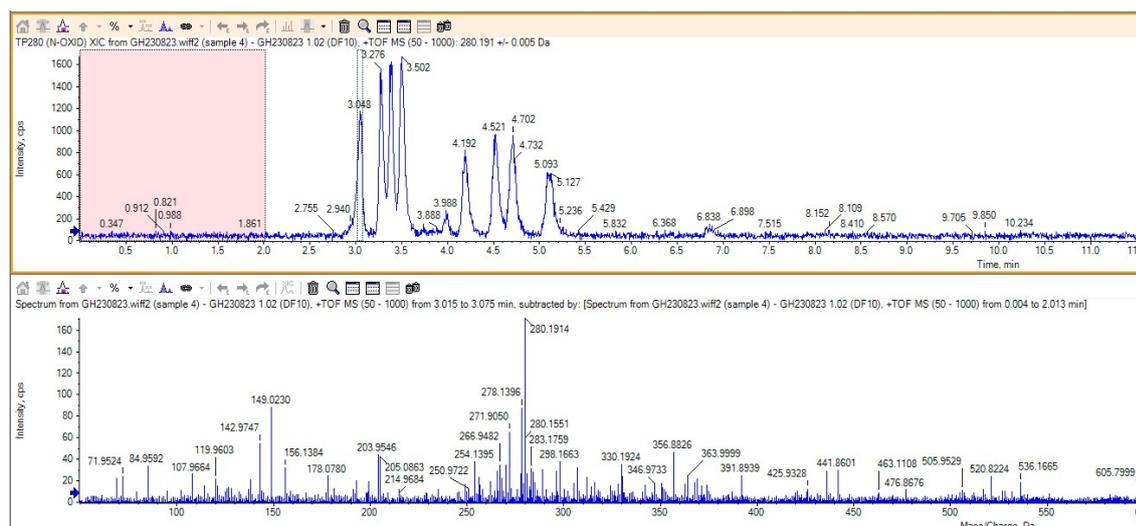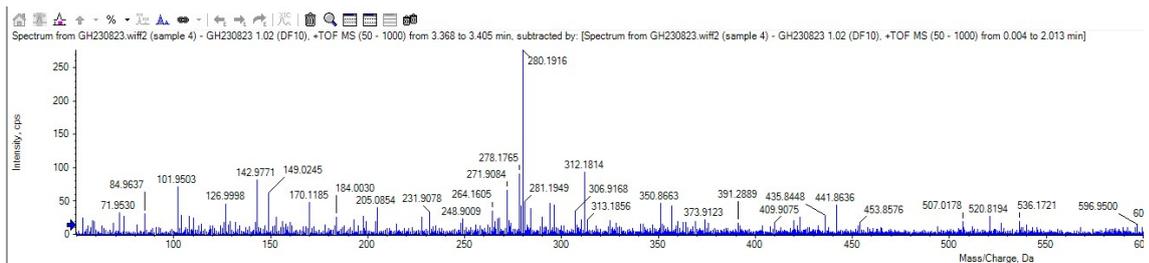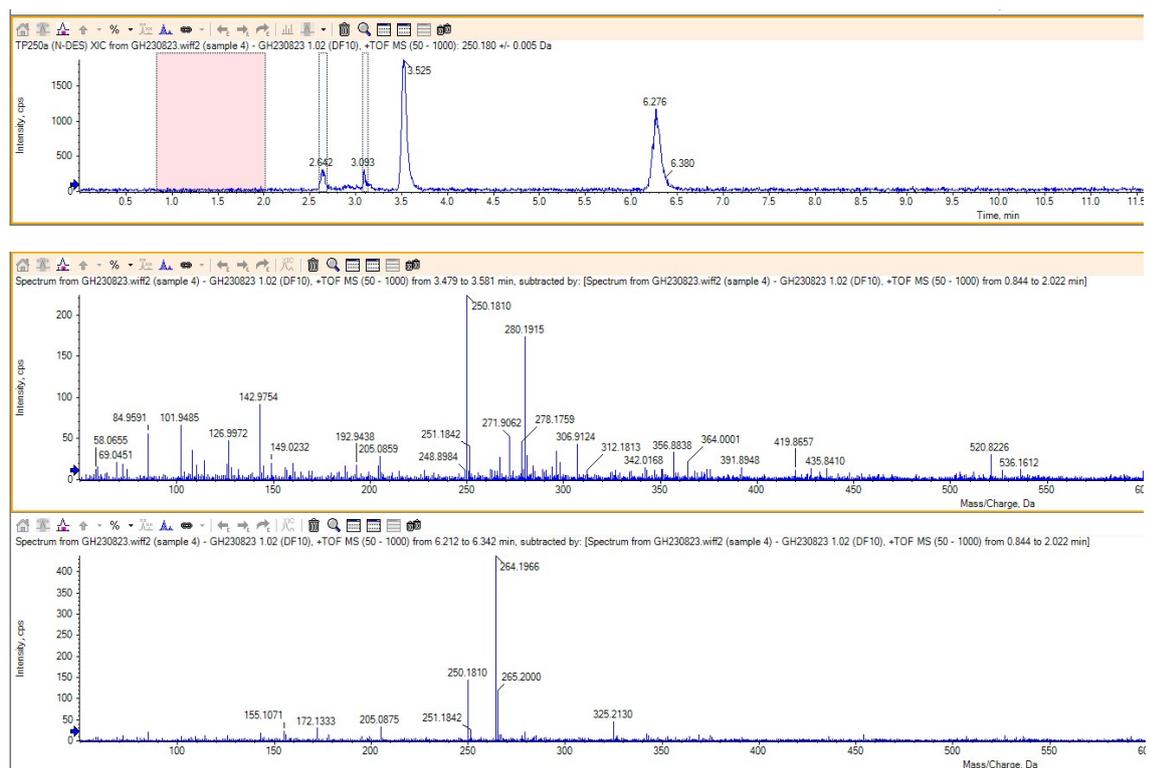
Fig. S7 The XIC for TP280 (C$_{16}$H$_{25}$NO$_3$), m/z = 280.1907, width 0.01 Da, and the mass spectra for the peaks eluted at 3.048 and 3.394 min (continued in Fig. S8)
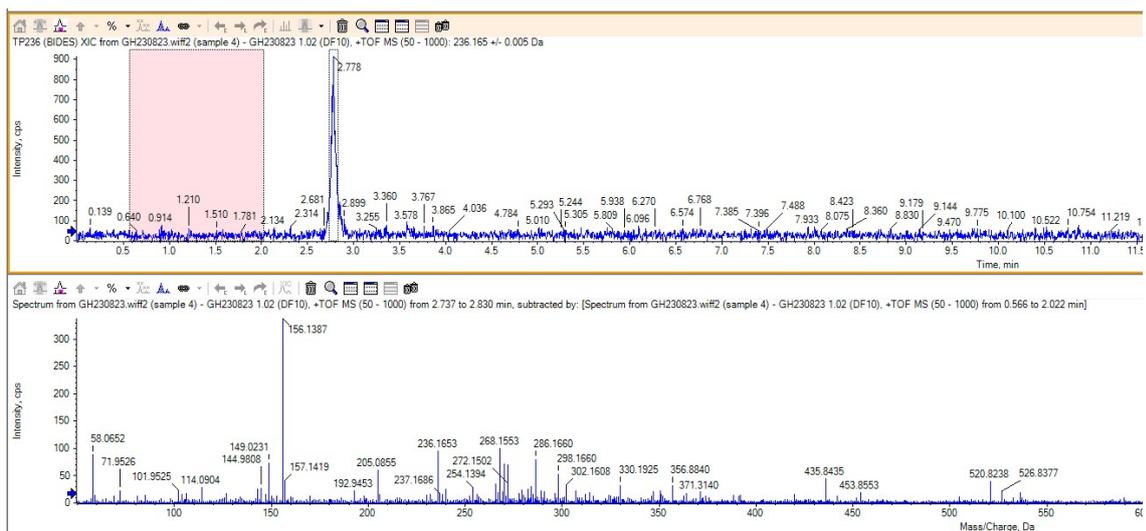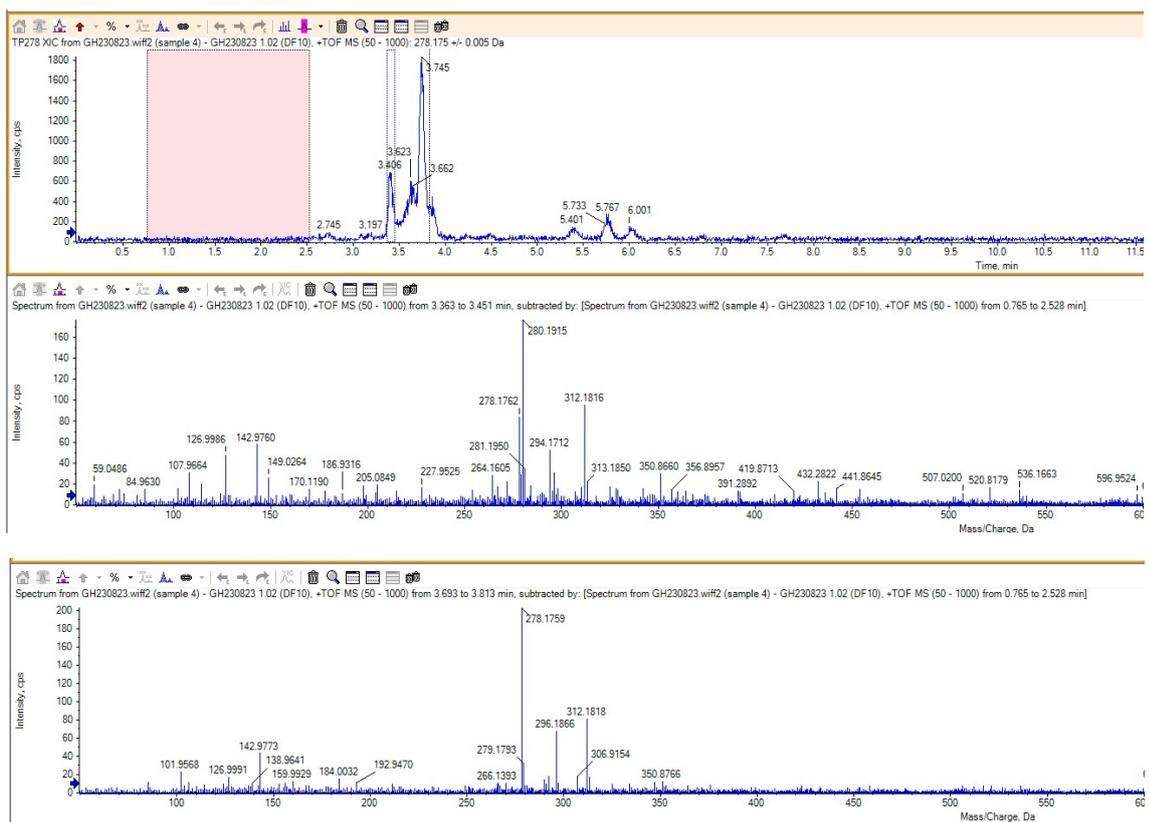
Fig. S8 (continued) The XIC for TP280 ($C_{16}H_{25}NO_3$), m/z = 280.1907, width 0.01 Da, and the mass spectra for the peaks eluted at 3.502, 3.988, 4.192, 4.521, 4.702, and 5.093 min
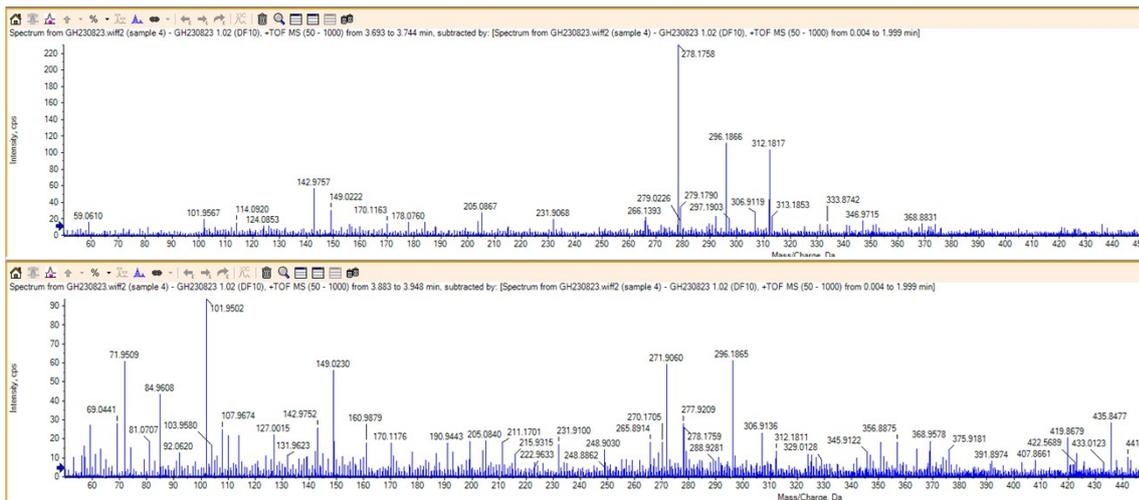

Fig. S9 The XIC for ($C_{16}H_{23}NO_3$), m/z = 250.1802, width 0.01 Da, and the mass spectra for the peaks eluted at 3.525 and 6.276 min
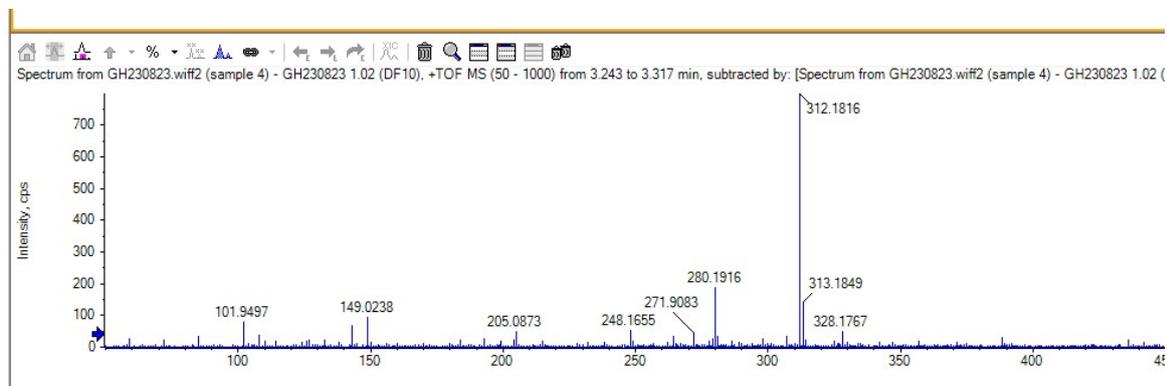
Fig. S10 The XIC for (C$_{14}$H$_{21}$NO2), m/z = 236.1645, width= 0.01 Da, and the mass spectrum for the peak eluted at 2.778 min

Fig. S11 The XIC for (C$_{16}$H$_{23}$NO$_3$), m/z = 278.1751, width= 0.01 Da, and the mass spectra for the peaks eluted at 3.406 and 3.745 min

Fig. S12 The mass spectra for ($C_{16}H_{26}NO_4$), m/z = 296.1865, width= 0.01 Da, for the peaks eluted at 3.719 and 3.908 min

Fig. S13 The mass spectrum for ($C_{16}H_{26}NO_5$), m/z = 312.1816, width= 0.01 Da, for the peak eluted at 3.276 min

Table S4. Masses and prices of used persulfate based on available commercial prices

	Control (Batch)	Control (CFS)	Simulated Effluent (Batch)
n_{PS} (mol/reactor)	0.00014*	-	0.00014
m_{PS} (g/reactor)	0.03333	-	0.03333
n_{PS} (mol/m^3)	-	0.238**	-
m_{PS} (g/m^3)	95.23	56.65	95.23
Cost*** ($/m^3)	0.190	0.113	0.190

* $n = [PS] \times V = 0.4$ mM $\times 10^{-3} \times 0.35 = 0.14 \times 10^{-3}$ mol/reactor

** V_{PS} needed from 14 mM stock solution is 4 mL for every 235 mL of effluent; therefore, the volume needed for 1 m^3 of influent is 17022 mL.

          n_{PS} per m^3 of influent = 14×10^{-3} x $17022 \times 10^{-3} = 0.238$ mol

***   1 kg of PS costs $2 based on the price obtained from Jinan Shijitongda Chemical Co., Ltd