

Electronic Supporting Information for

**Investigating Naproxen Removal from Pharmaceutical Factory Effluents
Using UVA/MIL-88-A/PS and Solar/MIL-88-A/PS Systems**

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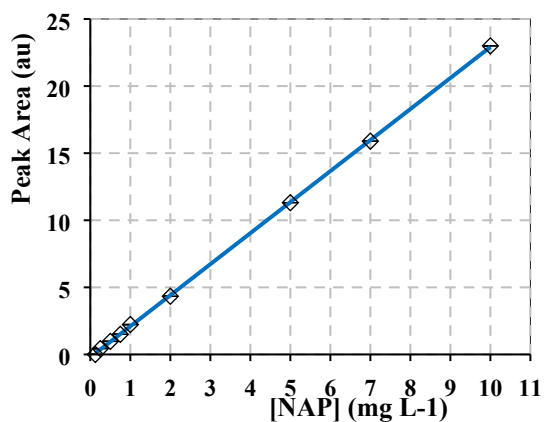
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Linest Output NAP			
y = mx + b			
m	2.312642	-0.21149	b
s _m	0.008292	0.037073	s _b
R ²	0.99991	0.083388	s _y

(a)

(b)

Fig. S1. (a) HPLC-DAD calibration curve for NAP. The error bars are calculated at 95% confidence level. Absorbance = $A(\text{mean}) \pm \frac{ts}{\sqrt{n}}$, where t is the student value (t = 2.447 for 6 degrees of freedom at 95% confidence level) and s the standard deviation of 7 replicates. (b) The LINEST output calculated through Excel provided the slope, y-intercept, the regression coefficient, and all statistical data including standard deviations on variables.

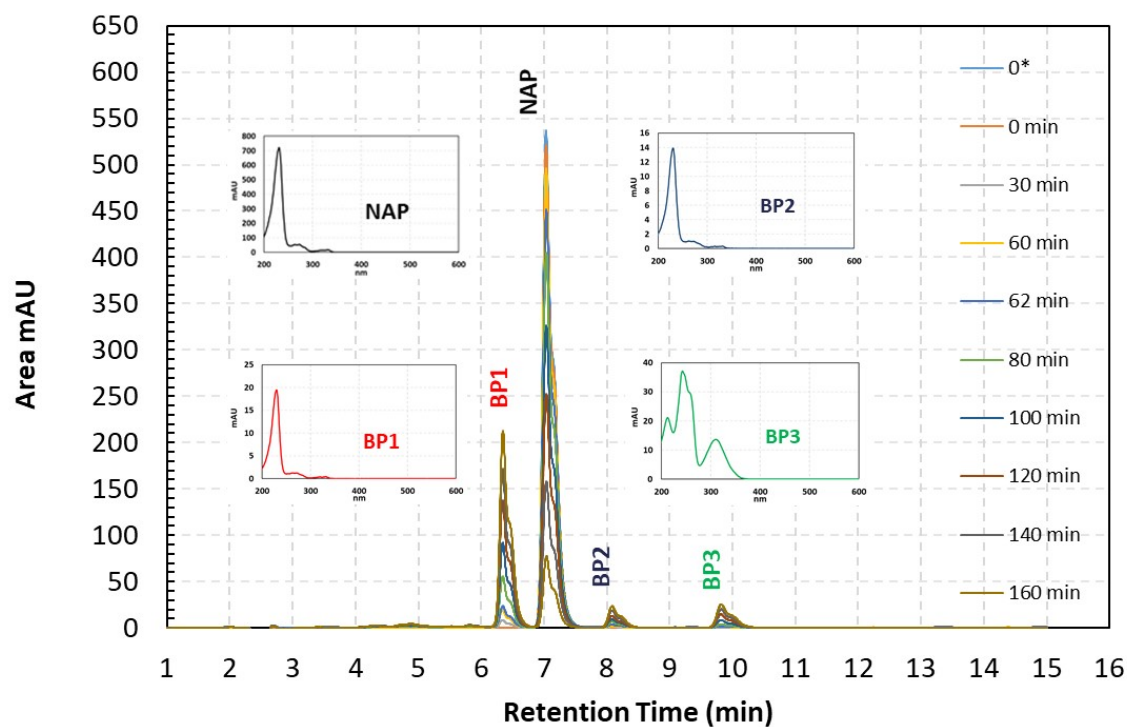


Fig. S2. Chromatogram of NAP extracted at 228 nm showing the by-products formed at 6.30, 8.06 and 9.79 min, respectively under UVA irradiation in UVA/MIL-88-A/PS system.

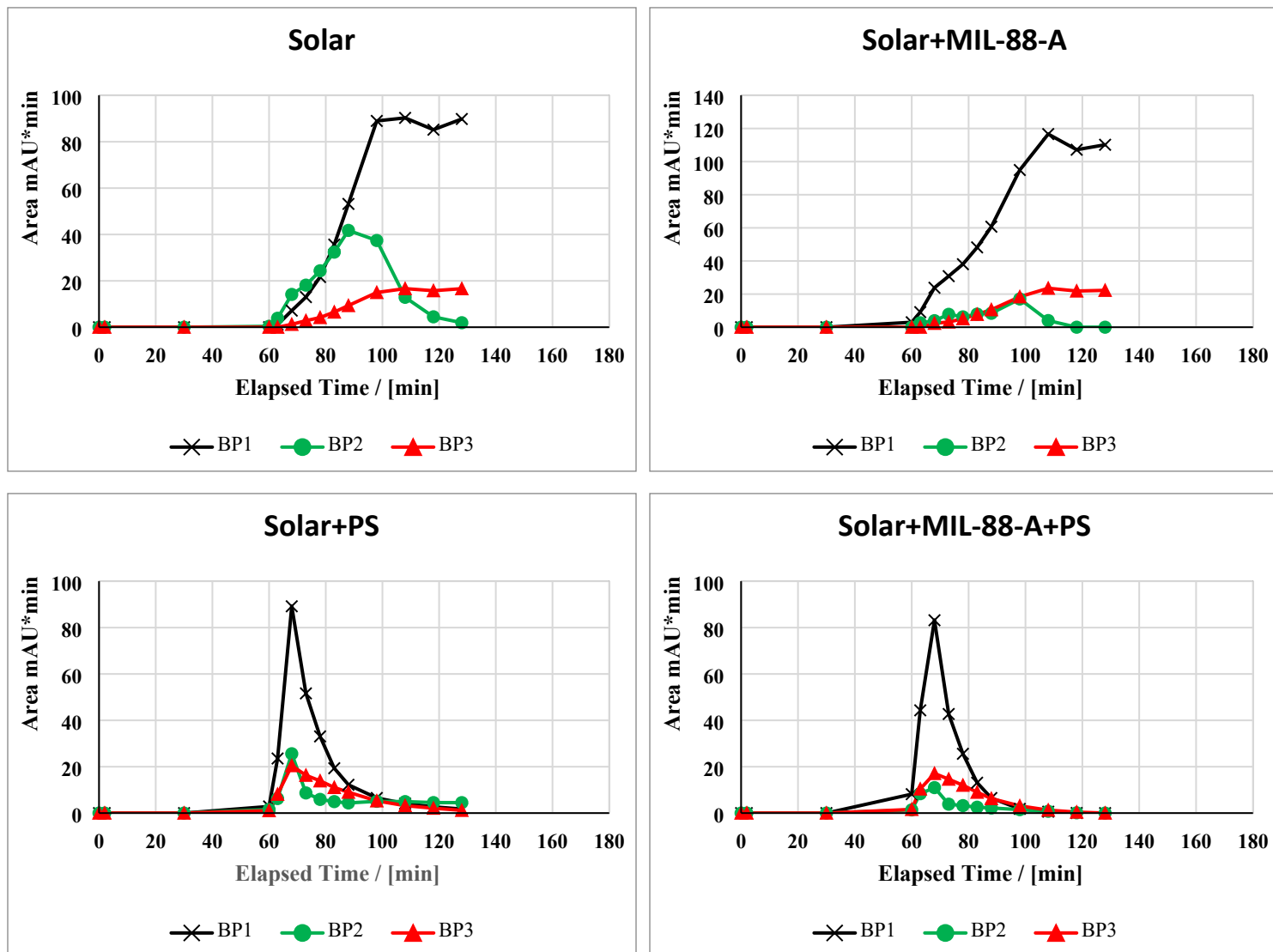


Fig. S3. Degradation by-products profile under different conditions: Solar/MIL-88-A/PS system control in the presence and/or absence of MIL-88-A and PS. Experimental conditions: $[NAP]_0 = 50 \text{ mg L}^{-1}$, $[PS]_0 = 2 \text{ mM}$, $[MIL-88-A]_0 = 25 \text{ mg L}^{-1}$.

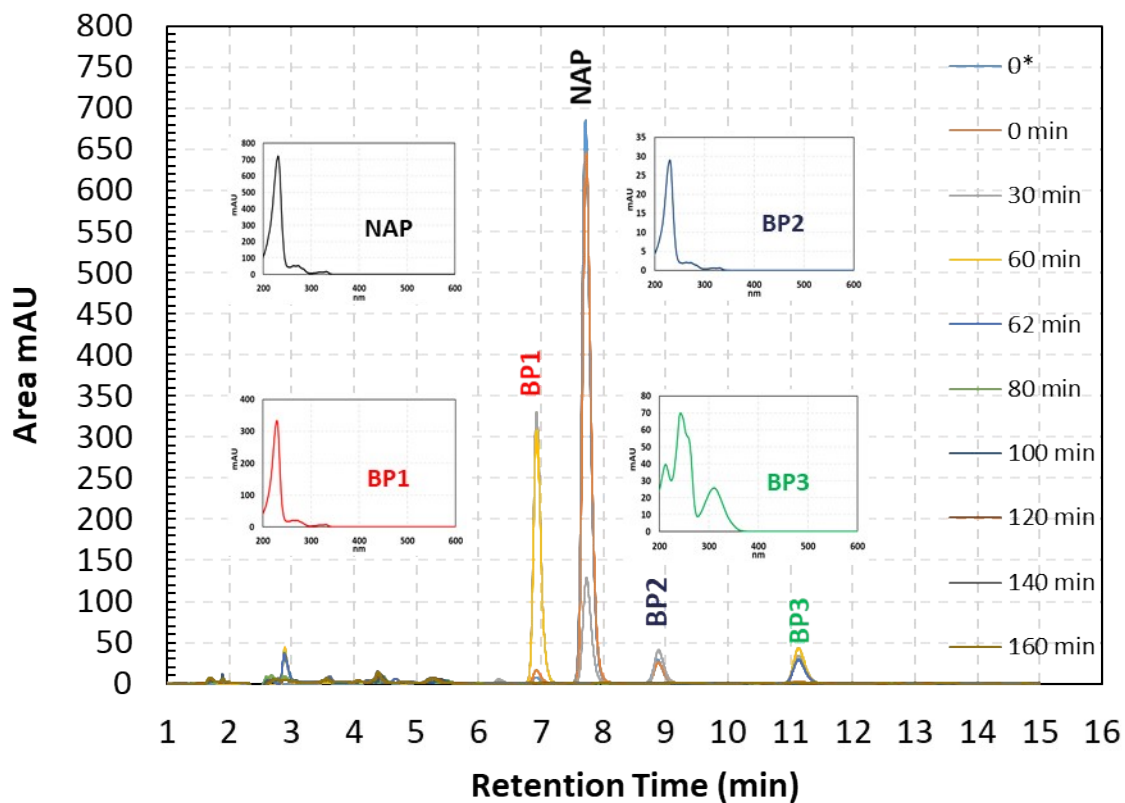


Fig. S4. Chromatogram of NAP extracted at 228 nm showing the by-products formed at 6.93, 8.73 and 11.13 min, respectively under Solar/MIL-88-A/PS system.

Table S1. pH values under different experimental conditions for the (a) UVA/MIL-88-A/PS/NAP system and (b) Solar/MIL-88-A/PS/NAP system

Case of chlorides		
(a) UVA system	pH initial	pH final
[NaCl] free	6.10	3.73
[NaCl] = 200 mg L ⁻¹	6.11	4.24
[NaCl] = 2000 mg L ⁻¹	5.72	4.29
[NaCl] = 20 000 mg L ⁻¹	5.79	4.56
(b) Solar system		
(a) UVA system	pH initial	pH final
[NaCl] free	6.12	2.51
[NaCl] = 200 mg L ⁻¹	6.85	2.59
[NaCl] = 2000 mg L ⁻¹	6.41	2.78
[NaCl] = 20 000 mg L ⁻¹	6.49	2.93
Case of phosphates (phosphate buffer (PB) at pH=4)		
(a) UVA system	pH initial	pH final
[PB] free	6.10	3.73
[PB] = 1 mM	5.41	4.32
[PB] = 5 mM	4.91	4.3
[PB] = 10 mM	4.66	4.25
(b) Solar system		
(a) UVA system	pH initial	pH final
[PB] free	6.12	2.51
[PB] = 1 mM	5.81	2.99
[PB] = 5 mM	5.11	3.16
[PB] = 10 mM	4.83	3.27
pH effect (10 mM phosphate buffer)		
(a) UVA system	pH initial	pH final
control	6.10	3.73
[pH] = 4	4.68	4.28
[pH] = 7	7.39	7.34
[pH] = 9	8.82	8.41
(b) Solar system		
(a) UVA system	pH initial	pH final
control	6.12	2.51
[pH] = 4	4.63	3.20
[pH] = 7	7.23	7.08
[pH] = 9	8.51	7.50

Case of bicarbonates		
(a) UVA system	pH initial	pH final
$[HCO_3^-]$ free	6.10	3.73
$[HCO_3^-] = 1 \text{ mM}$	8.05	7.02
$[HCO_3^-] = 50 \text{ mM}$	8.59	8.54
$[HCO_3^-] = 100 \text{ mM}$	8.56	8.59
(b) Solar system		
(b) Solar system	pH initial	pH final
$[HCO_3^-]$ free	6.12	2.51
$[HCO_3^-] = 1 \text{ mM}$	8.09	2.88
$[HCO_3^-] = 50 \text{ mM}$	9.04	8.78
$[HCO_3^-] = 100 \text{ mM}$	8.84	8.91

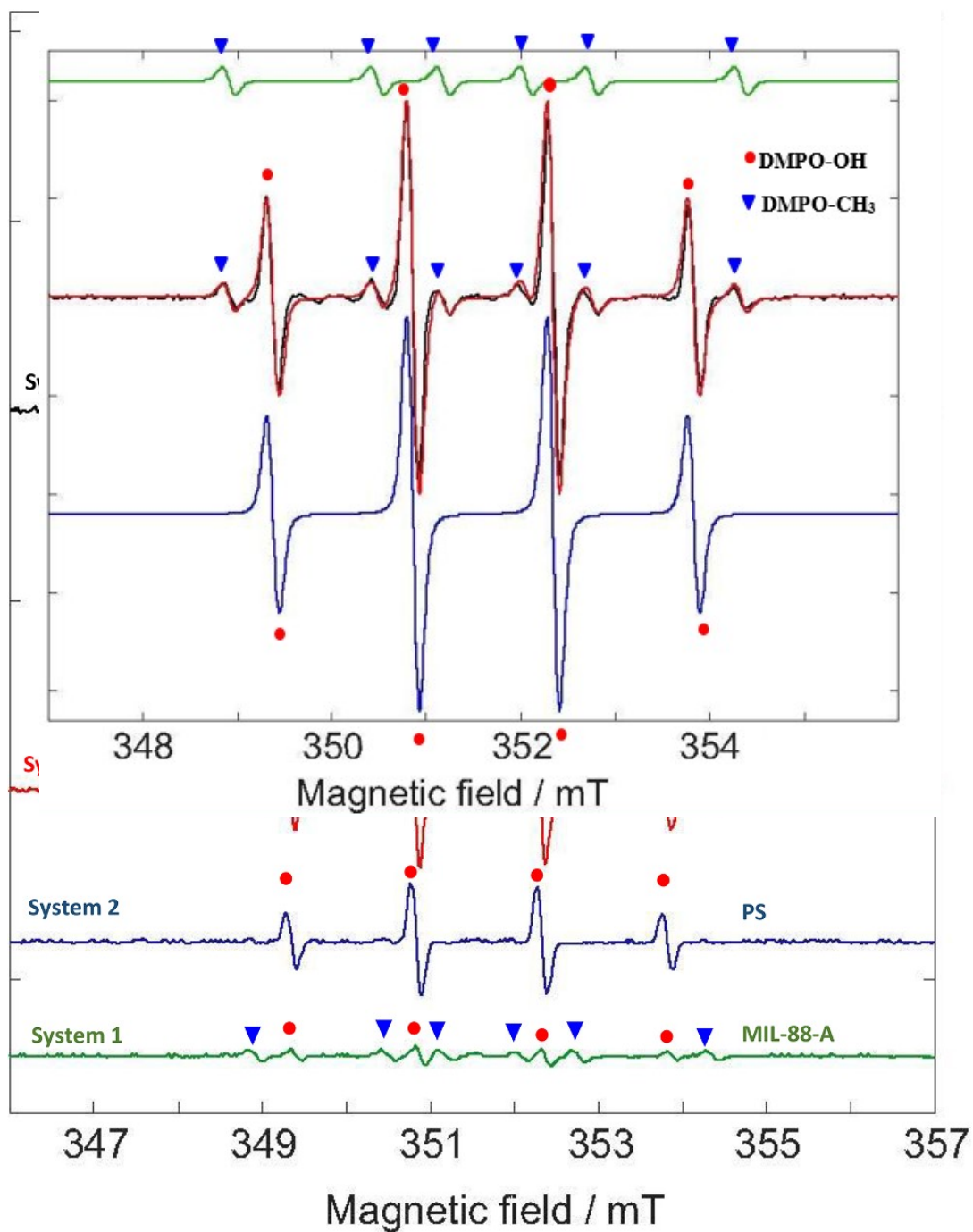


Fig. S5. EPR spectra of DMPO-radical adducts in different reaction systems. Experimental conditions: [PS] = 2.5 mM, [MIL-88-A] = 12.5 mg L⁻¹, [DMPO] = 100 mM. The acquisition duration of EPR spectra is about 100 min for all systems.

Fig. S6. EPR spectra. Green – simulated EPR spectrum for trapped methyl radicals. $a_N = 1.58$ mT, $a_H = 2.28$ mT. Blue – simulated EPR spectrum for trapped hydroxyl radicals. $a_N = 1.49$ mT, $a_H = 1.49$ mT. Red – the sum of the above two simulated trapped radical spectra. Black – experimental EPR spectrum under the following Experimental conditions: [PS] = 2.5 mM, [MIL-88-A] = 12.5 mg L⁻¹, [DMPO] = 100 mM.

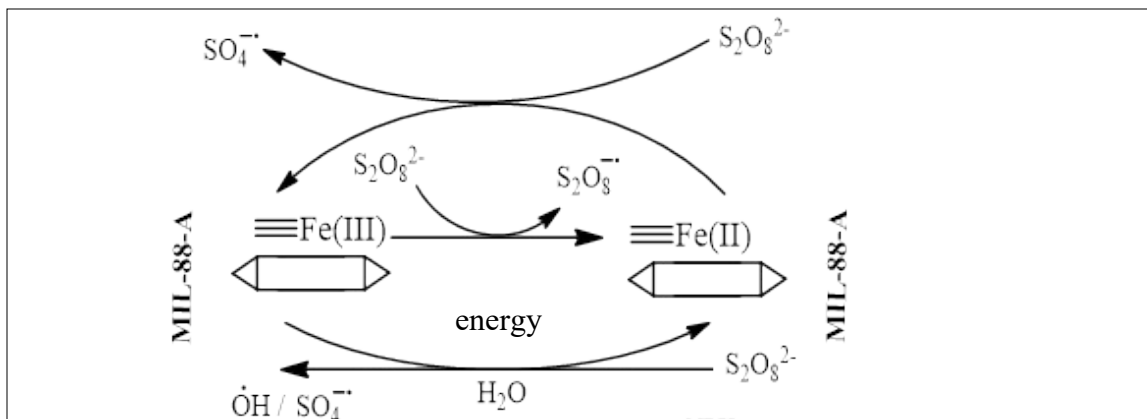


Fig. S7. Activation mechanism of PS in the UVA/MIL-88-A system

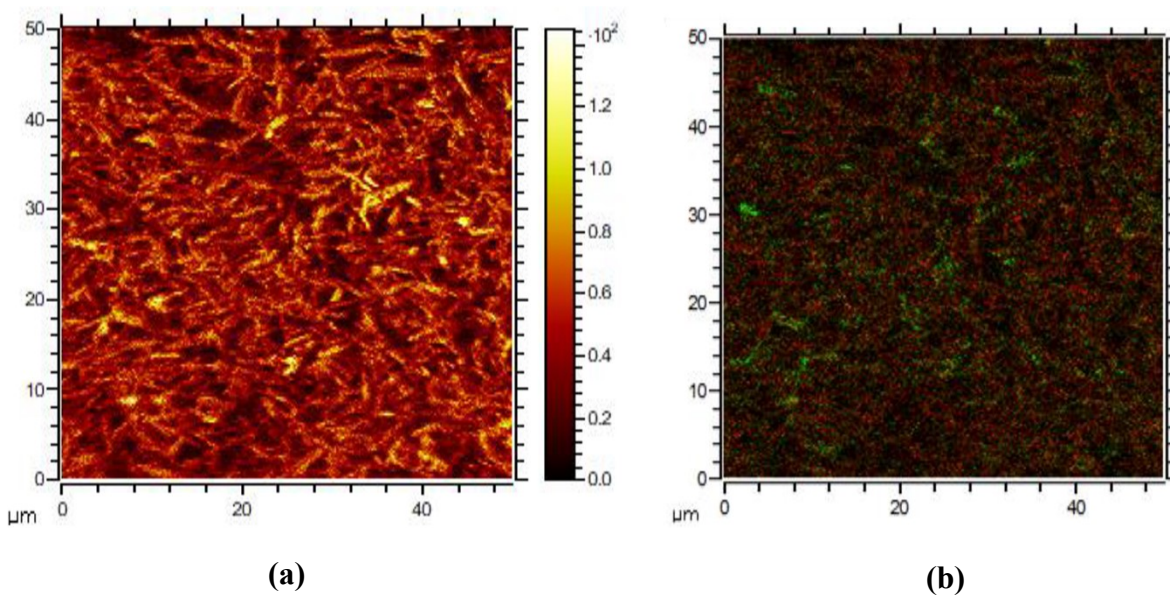


Fig. S8. TOF-SIMS characterization results: (a) Image of the sum of all positive secondary ions of the MIL-88-A as prepared in the presence of NAP and PS at $t = 80$ min. The color scale goes from black (lack of emission) to white (saturated emission). (b) Overlay of the characteristic peak of MIL-88-A, Fe^+ ion at m/z 56 image (red color) and the characteristic peak of decarboxylated NAP at m/z 185.0961 image (green color).