MILL88-A as a Mediator for the Degradation of Sulfamethoxazole in PS Systems: Implication of Solar Irradiation for Process Improvement

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Supplementary Material

12 Pages, 3 Textes, 19 Figures, 3 Tables

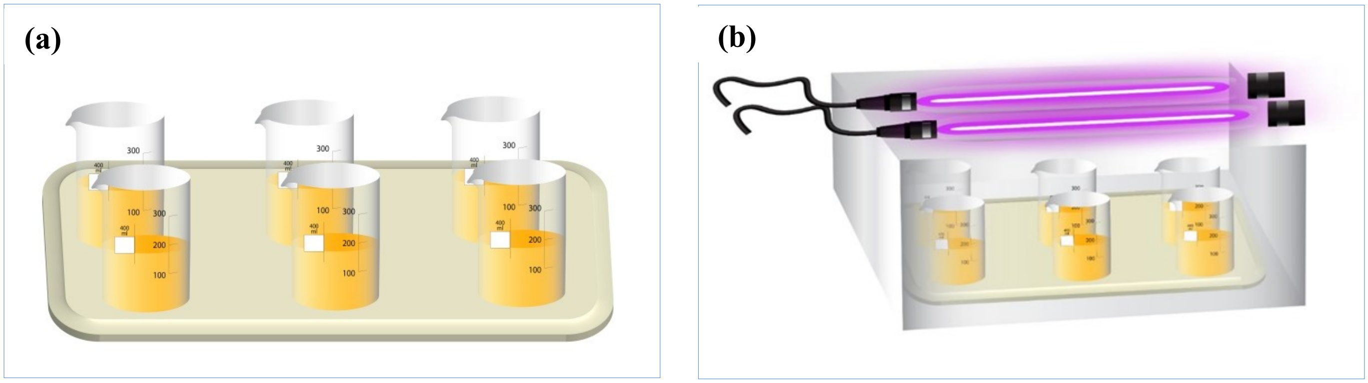


Fig. S1. Experimental Setup: six beakers are used as reactors for the performance of SMX removal in UVA/MIL88-A/PS system where two UVA mosquito lamps are used for irradiating the solution from the top.

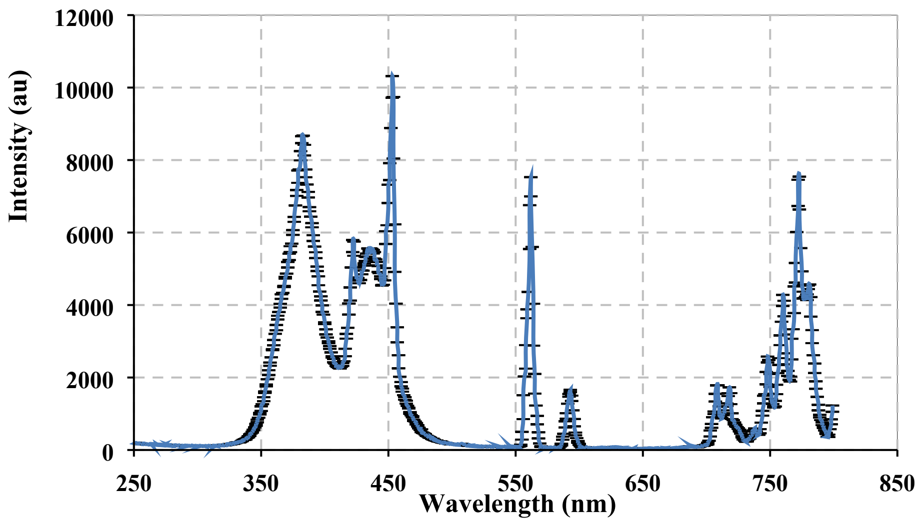


Fig. S2. Emission spectrum of the UV-A lamps used in this experiment.

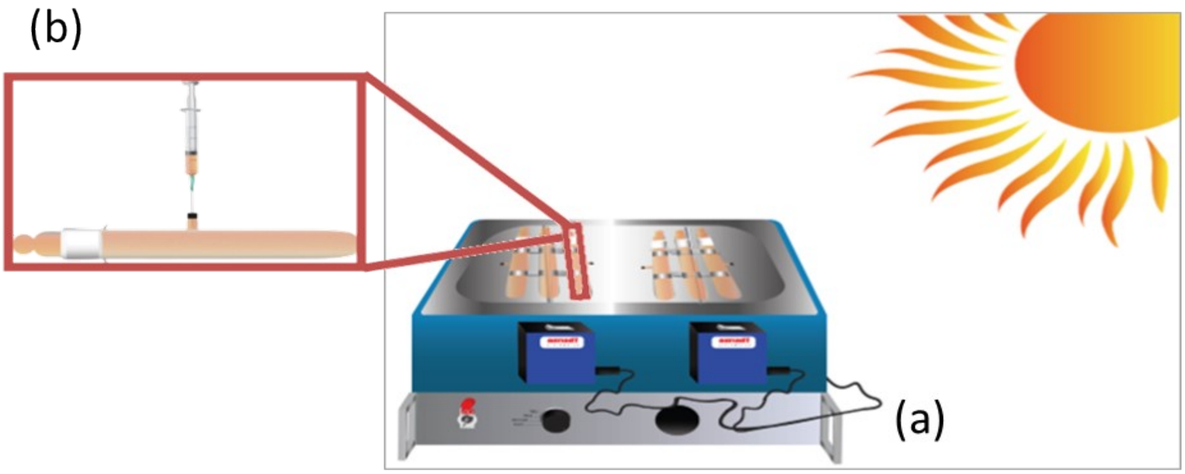
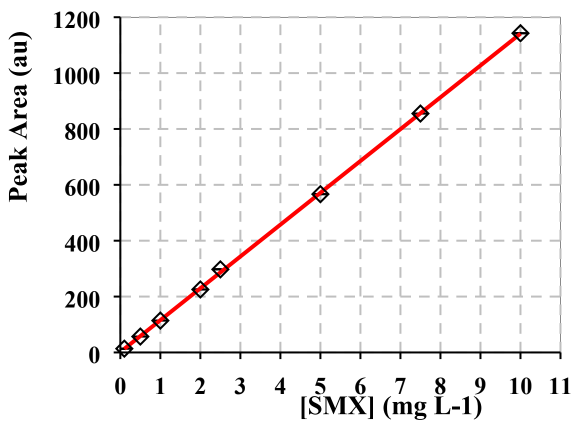


Fig. S3. (a) Reactors used in the Solar/MIL88-A/PS/SMX system (b) top view of experimental setup of experiments done under solar irradiation and a single reactor from the rotisserie shaker irradiated system with the syringe showing the sample collecting process.



Linest Output SMX			
y = mx + b			
m	113.9558	1.578785	b
s_m	0.552732	2.713177	s_b
R^2	0.999859	5.258659	s_y

(a) (b)

Fig. S4. (a) Calibration curve of SMX. The error bars are calculated at 95% confidence level. Absorbance = A (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 8 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.

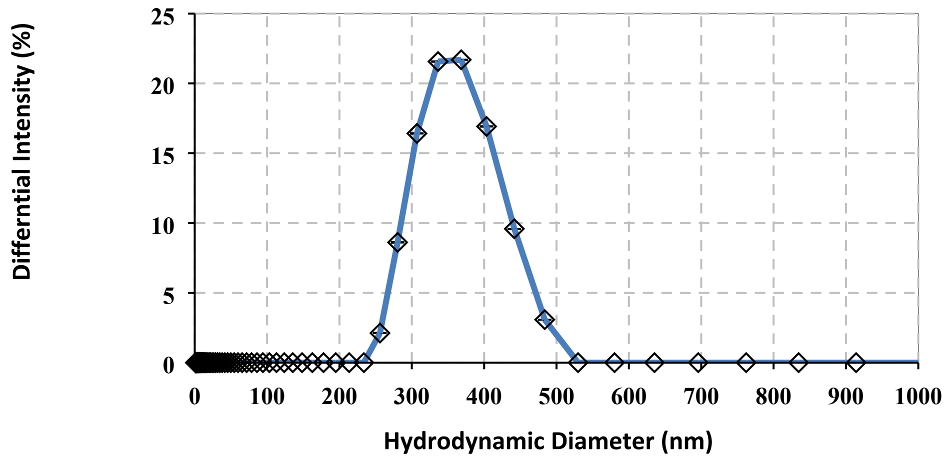


Fig. S5. Hydrodynamic diameter distribution profile of the synthesized MIL88-A determined using DLS.

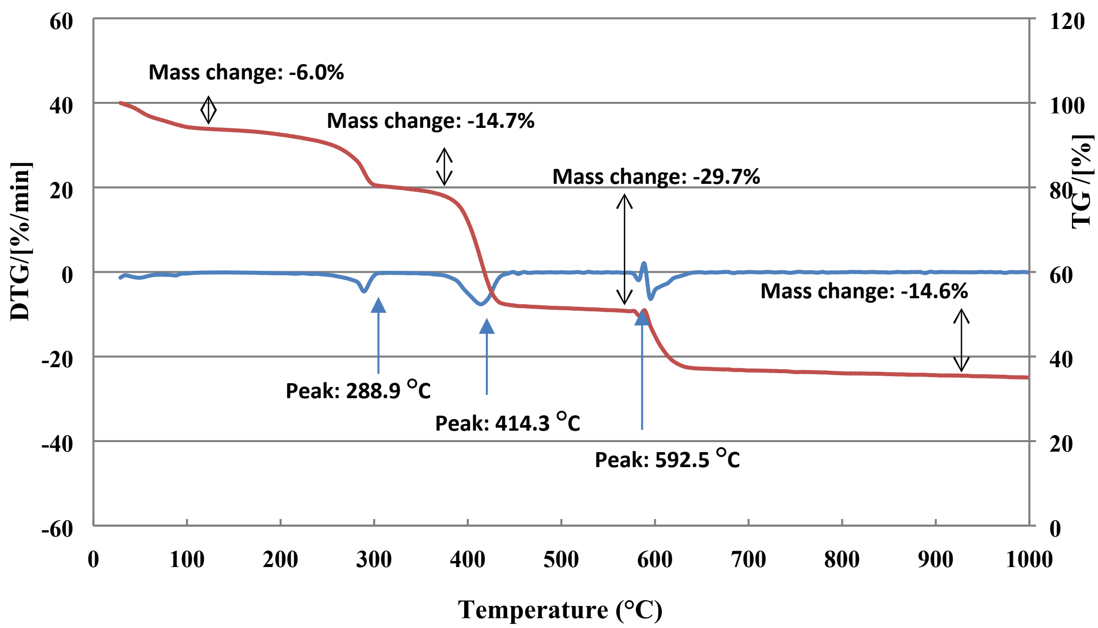


Fig. S6. Thermogravimetric analysis (TGA) of MIL88-A.

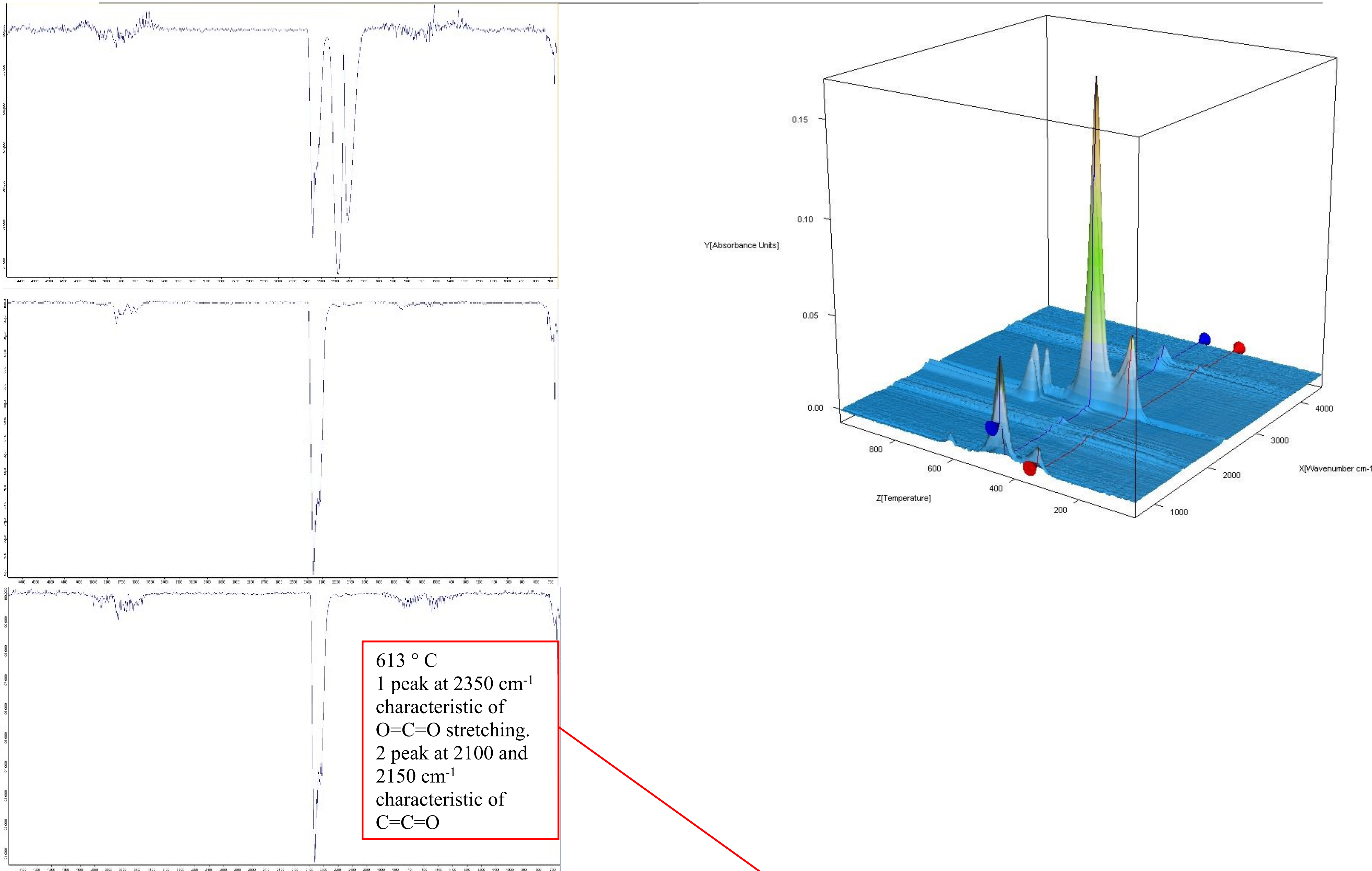


Fig. S7. TGA-FTIR analysis of the synthesized MIL88-A.

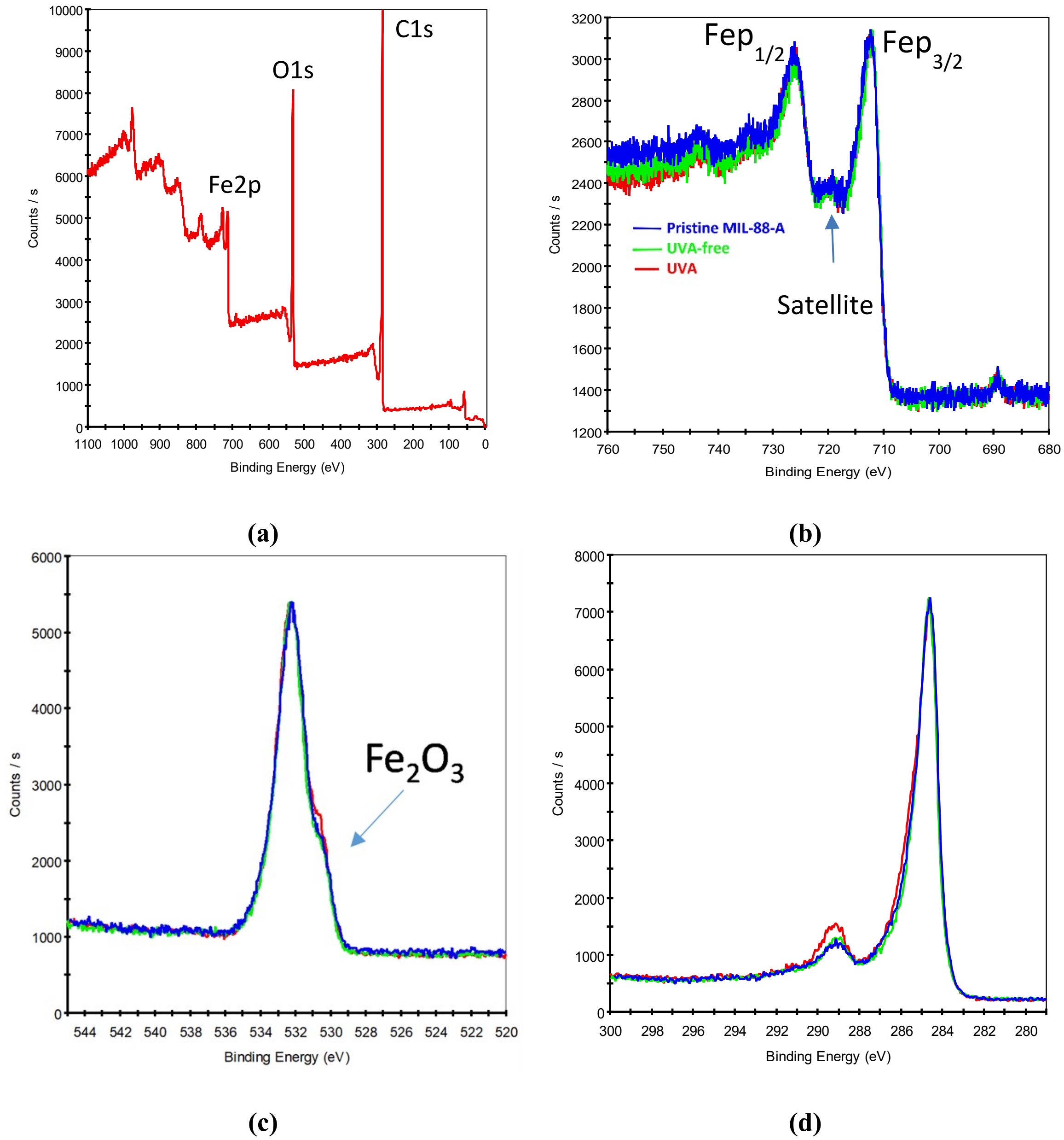


Fig. S8 XPS analysis of pristine MIL88-A and used MIL88-A in UVA-free and UVA-irradiated systems after the oxidation reaction. (a) XPS survey spectra, (b) Fe2p$_{3/2-1/2}$ spectra, (c) O1s spectra and (d) C1s spectra. XPS spectra of all samples are almost overlapping everywhere with no significant difference.

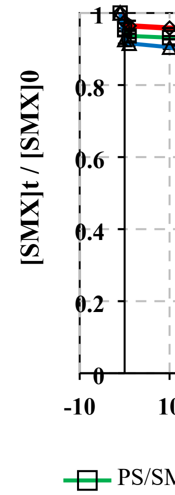


Fig. S9 Elimination of SMX by MIL88-A in the presence and in the absence of PS as well as with PS only in beakers on top of a multi-stirrer. Experimental conditions: $[SMX]_0 = 10$ ppm, $[PS]_0 = 2$ mM, $[MIL88\text{-}A]_0 = 250$ mg L^{-1}. Vertical bars represent standard deviations of the means; absent bars fall within symbols. Sample before t = 0 min was taken before the addition of PS; PS addition at t_0.

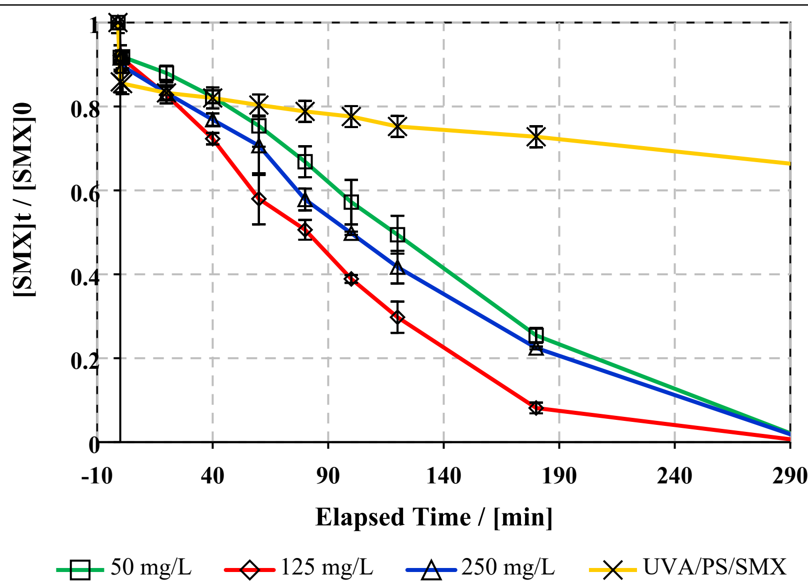


Fig. S10 The % degradation of SMX as function of time (min) using three different masses of MIL88-A (50 mg, 25 mg and 10 mg) are plotted against the control experiment (UVA/PS/SMX system, upper curve). Experimental conditions: $[SMX]_0$ = 10 ppm, $[PS]_0$ = 2 mM, vertical bars represent standard deviations of the means; absent bars fall within symbols. Sample before t = 0 min was taken before the addition of PS, PS addition at t_0.

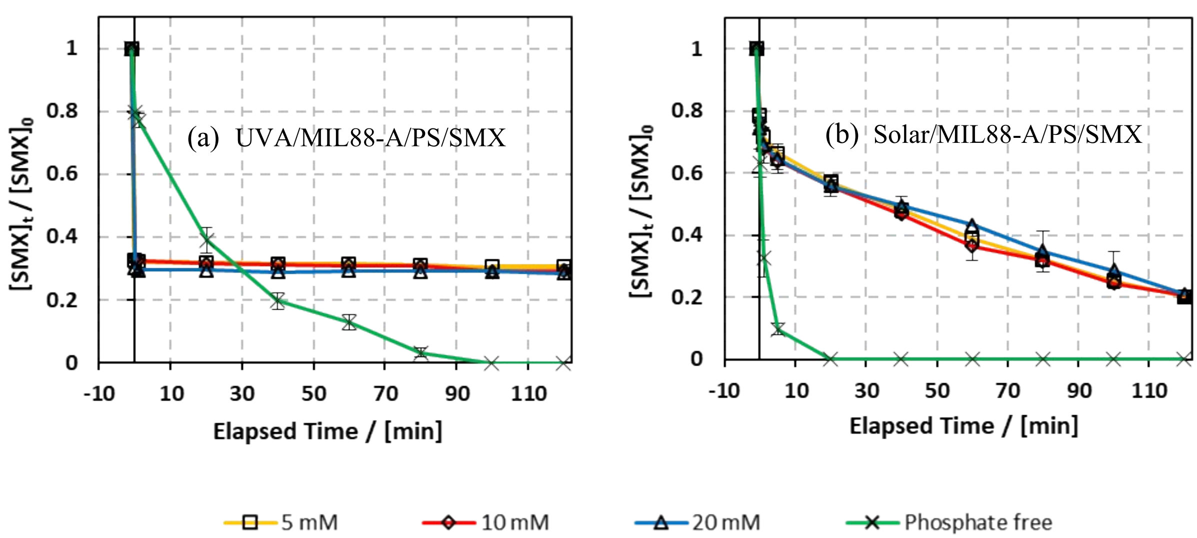


Fig. S11 Effect of phosphate concentration on the degradation of SMX as function of time (min): (a) in the UVA/MIL88-A/PS/SMX system and (b) in the solar/MIL88-A/PS/SMX system.

Experimental conditions $[PO_4^{3-}]$ = 5 - 20 mM, $[SMX]_0$= 5 ppm, $[PS]_0$ = 2 mM, $[MIL88\text{-}A]_0$= 125 mg L^{-1}. Error bars are calculated as $\frac{ts}{\sqrt{n}}$ where absent bars fall within the symbols.

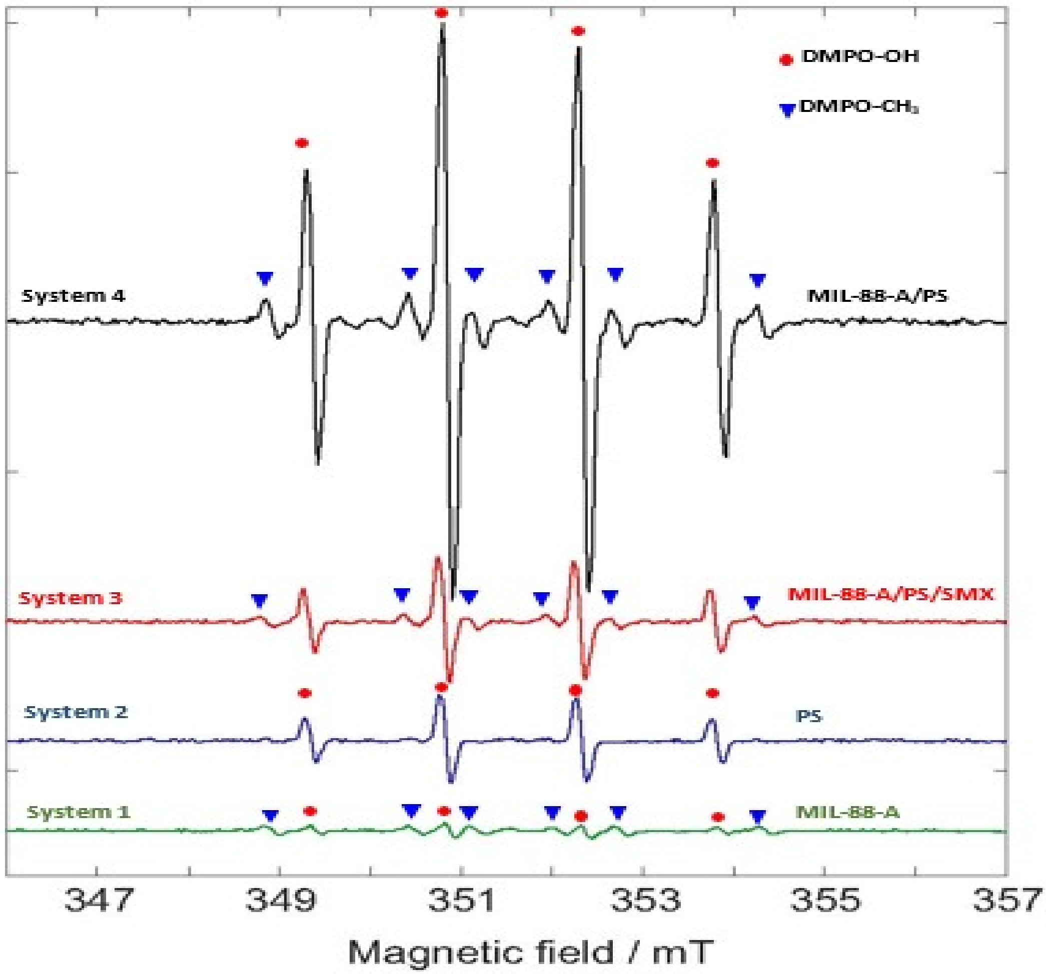


Fig. S12. EPR spectra of DMPO-radical adducts in different reaction systems. Experimental conditions: [PS] = 2.5 mM, [MIL88-A] = 12.5 mg L^{-1}, [DMPO] = 100 mM. The acquisition duration of EPR spectra is about 100 min for all systems.

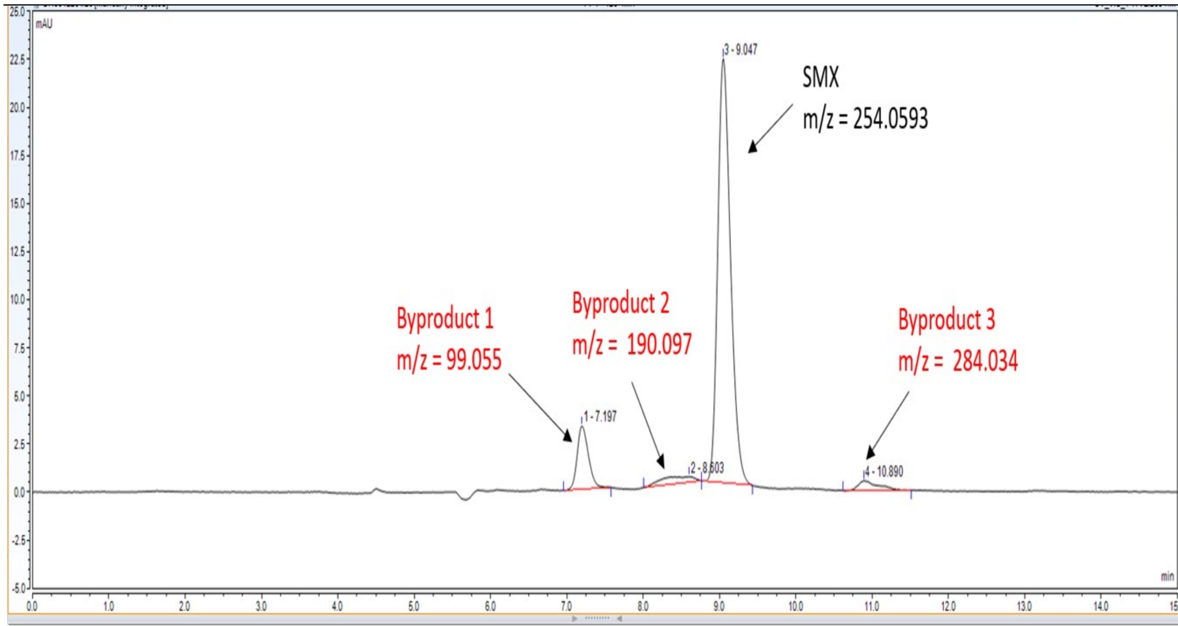


Fig. S13. HPLC chromatogram at T = 25 °C showing SMX and its byproducts at reaction time t= 40 mins

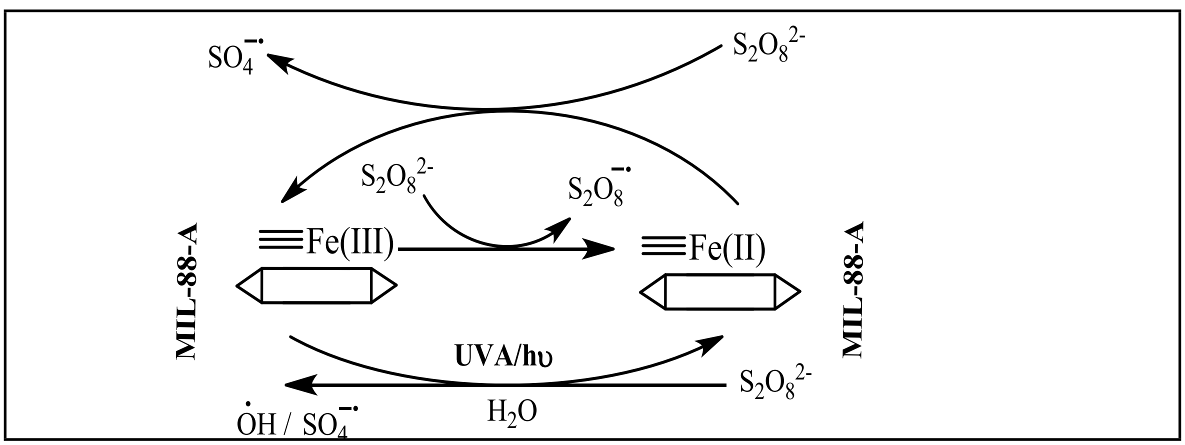


Fig. S14. Activation mechanism of PS in the UVA/MIL88-A system

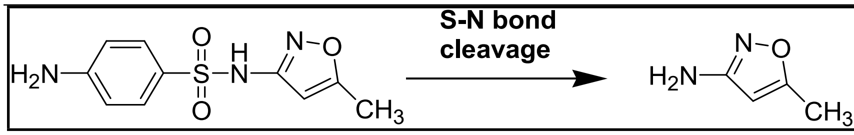


Fig. S15. Formation mechanism of BP**1**.

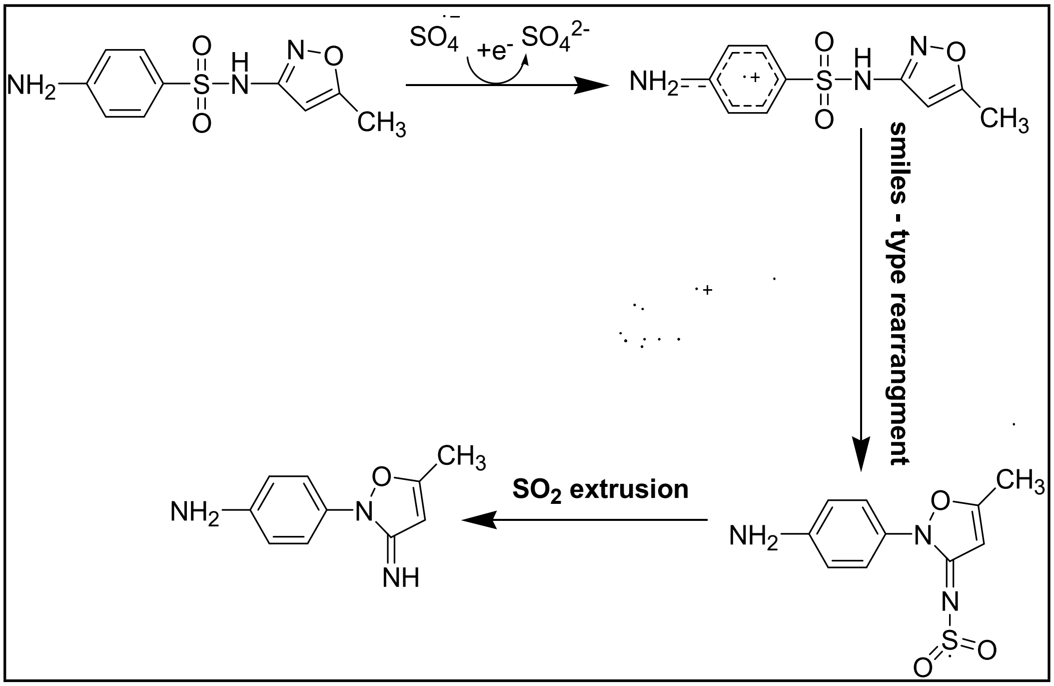


Fig. S16. Formation mechanism of BP**2**.

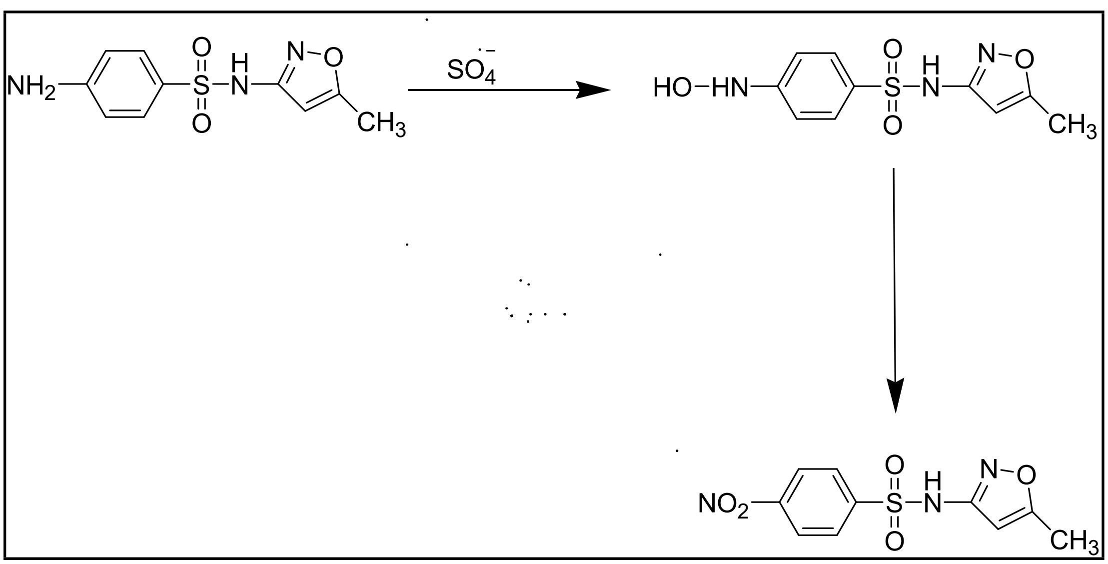


Fig. S17. Formation mechanism of BP**3**.

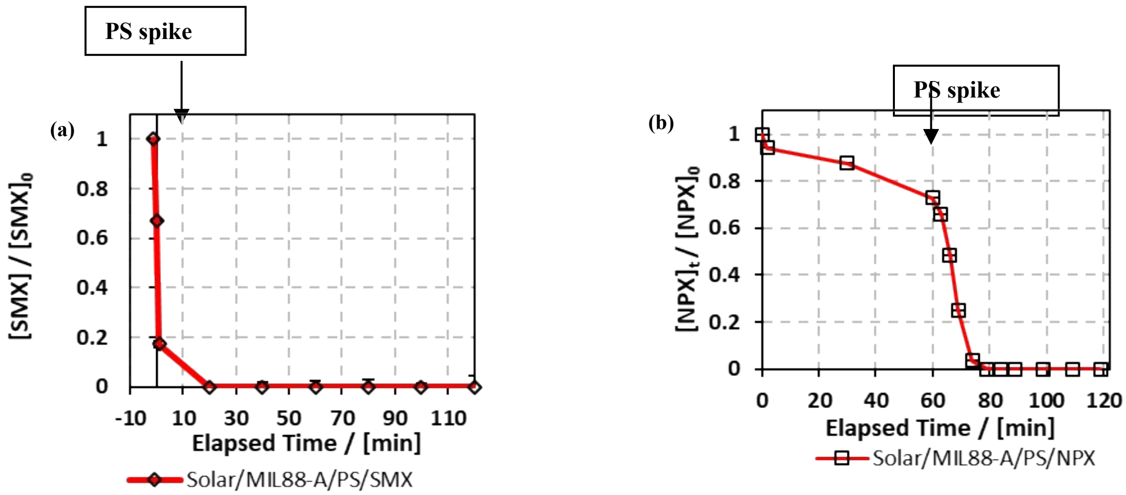


Fig. S18. Graph showing the effect of the solar/MIL88-A/PS on the degradation of (a) SMX and (b) NPX. Experimental conditions $[NPX]_0 = 50$ ppm, $[SMX]_0 = 5$ ppm, $[PS]_0 = 2$ mM, $[MIL88\text{-}A]_0 = 125$ mg L^{-1}. Error bars are calculated as $\frac{ts}{\sqrt{n}}$ where absent bars fall within the symbols.

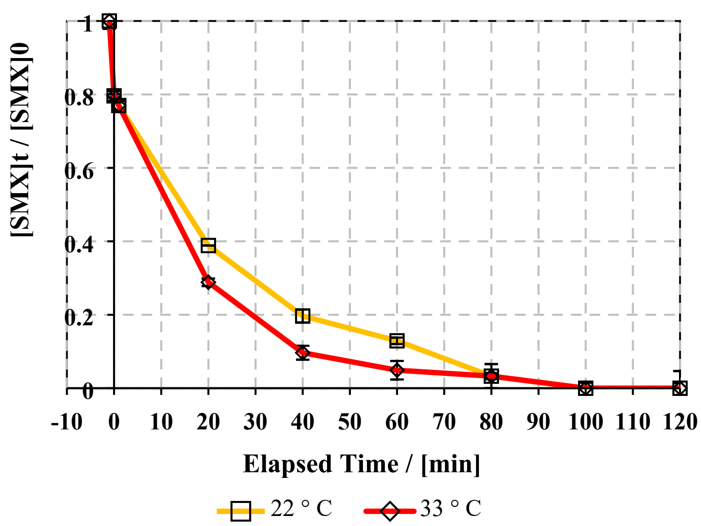


Fig. S19. Graph showing the effect of the solar/MIL88-A/PS on the degradation of SMX. Experimental conditions $[SMX]_0 = 5$ ppm, $[PS]_0 = 2$ mM, $[MIL88\text{-}A]_0 = 125$ mg L^{-1}. Error bars are calculated as $\frac{ts}{\sqrt{n}}$ where absent bars fall within the symbols.

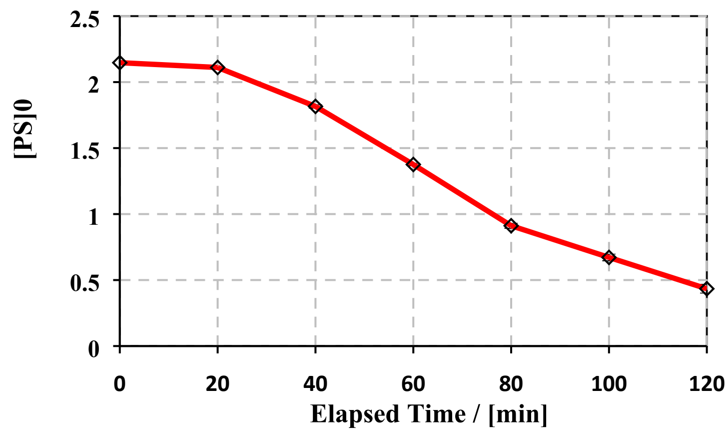


Fig. S20. Graph showing the [PS] as function of reaction time. Experimental conditions $[SMX]_0$ = 5 ppm, $[PS]_0$ = 2 mM, $[MIL88\text{-}A]_0$ = 125 mg L^{-1}. Error bars are calculated as $\frac{ts}{\sqrt{n}}$ where absent bars fall within the symbols.

Table S1
pH values of the different reaction systems during the experiment in (a) the UVA/MIL88-A/PS/SMX system and (b) the Solar/MIL88-A/PS/SMX system

(a) UVA system	pH initial	pH final
[HCO_3^-] free	3.53	3.29
[HCO_3^-] = 1 mM	6.46	5.31
[HCO_3^-] = 50 mM	8.57	8.87
[HCO_3^-] = 100 mM	8.66	8.86
(b) Solar System	**pH initial**	**pH final**
[HCO_3^-] free	3.52	3.15
[HCO_3^-] = 1 mM	6.18	5.19
[HCO_3^-] = 50 mM	8.31	8.37
[HCO_3^-] = 100 mM	8.40	8.42

Table S2
pH values of the different reaction systems during the experiment in the (a) UVA/MIL88-A/PS/SMX system and (b) the Solar/MIL88-A/PS/SMX system

(a) UVA system	**pH initial**	**pH final**
[PB] free	3.52	3.53
[PO_4^{3-}] = 5 mM	3.72	3.29
[PO_4^{3-}] = 10 mM	3.80	3.72
[PO_4^{3-}] = 20 mM	3.85	3.79
(b) Solar System	**pH initial**	**pH final**
[PO_4^{3-}] free	3.52	3.51
[PO_4^{3-}] = 5 mM	3.42	3.22
[PO_4^{3-}] = 10 mM	3.61	3.78
[PO_4^{3-}] = 20 mM	3.71	3.72

Table S3.

Masses and prices of reagents used based on commercial prices where 1 kg of PS costs 2 US $[a], 1 Kg of $FeCl_3$ costs 3.33 US $[b], and 1 Kg of fumaric acid ($C_4H_4O_4$) costs 2.5 US $[c] in the UVA/MIL88-A/PS and solar/MIL88-A/PS sytems.

System	UVA/MIL88-A/PS	Solar/MIL88-A/PS
$[PS]_0$ mM	2	2
[MIL88-A] mg/L	25	25
Cost $ [MIL88-A]	1.76 x 10^{-4}	1.76 x 10^{-4}
Reactor volume L	0.2	0.1
n PS mol	0.0004	0.0002
m $Na_2S_2O_8$ g	0.00952	0.0476
Cost $ [PS]	1.904 x 10^{-4}	9.52 x 10^{-5}
Total cost $ reactor^{-1}	4 x 10^{-3}	2.76 x 10^{-4}
Total cost $ m^{-3}	24.6	2.76

[a] Based on price obtained from Jinan Shijitongda Chemical Co., Ltd.
[b] Based on price obtained from Gemhold (SJZ) Trading Co., Ltd.
[c] Based on price obtained from Hangzhou Focus Corporation.

Text 1. Effect of the studied system on the degradation of Naproxen

In an attempt to study the robustness of the solar/MIL88-A/PS system, a different contaminant was used under the same conditions. Naproxen (NPX), an NSAID, is chosen due to its frequent detection in aquatic systems as well as in drinking water [1] and resistance to traditional wastewater treatment methods. As it can be noticed from Fig. S18, adsorption of NPX took place before the spike with 2 mM PS and [NPX] decreased by 20% in the first 60 mins of the experiment. In contrast, [SMX] remained constant in the 2 h prior to spiking with PS and no adsorption occurred (Fig. 3b). After spiking with PS, a huge drop in the concentrations of both contaminants was observed: [SMX] showed 80% degradation in the 10 first mins while NPX degradation reached 78 % after 70 mins of reaction. Full degradation of SMX and NPX was attained after 20 and 80 mins respectively. This proves the reproducibility of the solar/MIL88-A/PS system which requires further optimization to be used on larger scale.

Text 2. Effect of temperature on the degradation of SMX.

To study the effect of temperature on the degradation of SMX in the solar/MIL88-A/PS system and establish whether thermal activation is playing a role in this rapid degradation, the temperature of the reaction mixture in the solar system was measured (33°C) and implemented under UVA irradiation. The heated UVA/MIL88-A/PS system showed a slight enhancement in SMX degradation rate but complete degradation is attained within 80 mins, which is the same total degradation time attained at room temperature (22 °C). This proves that no thermal activation of PS occurs at 33°C.

Text 3. PS quantification using modified HPLC unit

To quantify PS, an in-house validated analytical method developed by Baalbaki et al. [2] was used. The method was based on modifying the configuration of an HPLC unit permitting the formation of I_3^- complex which is detected at a wavelength of 352 nm by the DAD.

References

[1] K.Y. Andrew Lin, H.A. Chang, C.J. Hsu, Iron-based metal organic framework, MIL-88A, as a heterogeneous persulfate catalyst for decolorization of Rhodamine B in water, RSC Adv. (2015). https://doi.org/10.1039/c5ra01447f.

[2] A. Baalbaki, N. Zein Eddine, S. Jaber, M. Amasha, A. Ghauch, Rapid quantification of persulfate in aqueous systems using a modified HPLC unit, Talanta. 178 (2018) 237–245. https://doi.org/10.1016/j.talanta.2017.09.036.