Chemically and thermally activated persulfate for theophylline degradation and application to a pharmaceutical factory effluent

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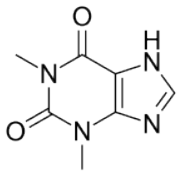
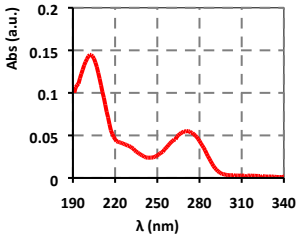
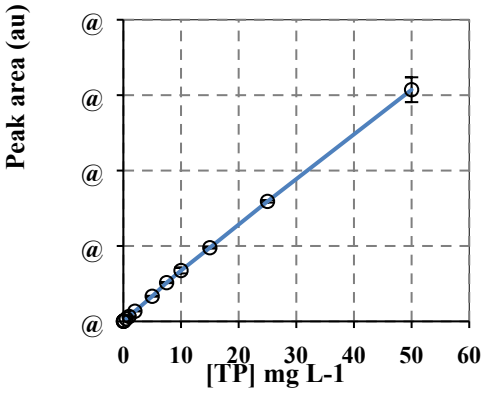
Electronic supplementary information

9 Pages, 3 Texts, 8 Figures, 2 Tables

(b)				(c)	
Chemical formula and CAS number	Chemical structure	Molecular weight (g mol^{-1})	pKa	Water solubility (mg mL^{-1})	Spectrum
$C_7H_8N_4O$ 58-55-9		180.164	8.81 [1]	8.3	



LINEST Output			
y=mx+b			
m	309.4	b	79.19
s_m	2.466	s_b	39.20
R^2	0.999	s_y	125.1

Fig. 1S. (a) Table showing selected TP chemical and physical properties. (b) Calibration curve of TP obtained using HPLC/DAD instrument at a wavelength of 270 nm, over a linear dynamic range of 0.02-50 mg L^{-1} with a detection limit = 0.0176 mg L^{-1} and quantification limit = 0.0586 mg L^{-1}. (c) LINEST output for TP calibration curve.

Text S1

Theophylline calibration curve

Selected TP physical properties are summarized in Fig. 1S (a). Calibration curve obtained for TP at a wavelength of 270 nm is presented in Fig. 1S(b). High linearity (R^2 = 0.999) is obtained over a linear dynamic range of 0.02-50 mg L^{-1} with a detection limit = 0.0176 mg L^{-1} and quantification limit = 0.0586 mg L^{-1}. Error bars for calibration curve are calculated as $A = A_{average} \pm \frac{ts}{\sqrt{n}}$, where n is the number of replicates, t is student value for 95%

confidence (t = 4.303 for 2 degrees of freedom) and s is the standard deviation of the three replicates tested.

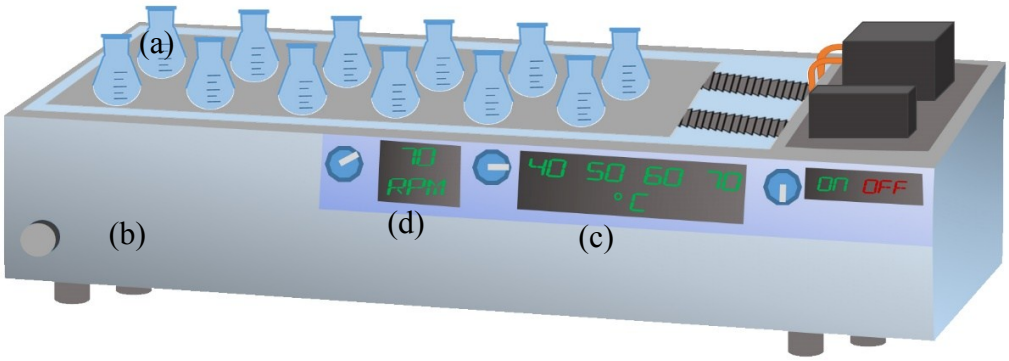


Fig. 2S. Experimental setup showing (a) reactors in (b) water bath equipped with (c) temperature control, and (d) automatic shaker. Temperature is displayed in °C and shaker in revolutions per minute (RPM).

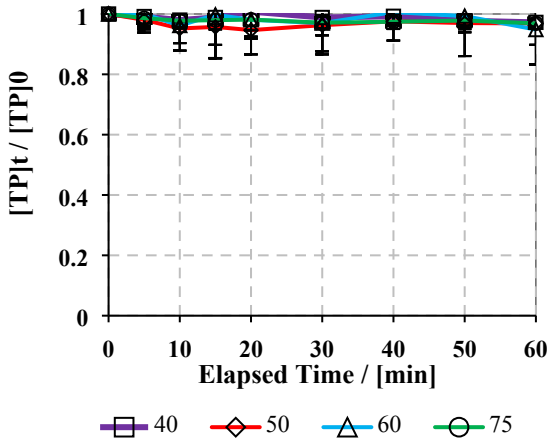


Fig. 3S. Stability of TP under heat stress. Experimental conditions: $[TP]_0$ = 10 mg L^{-1}, Temperature = 40, 50, 60 and 75°C.

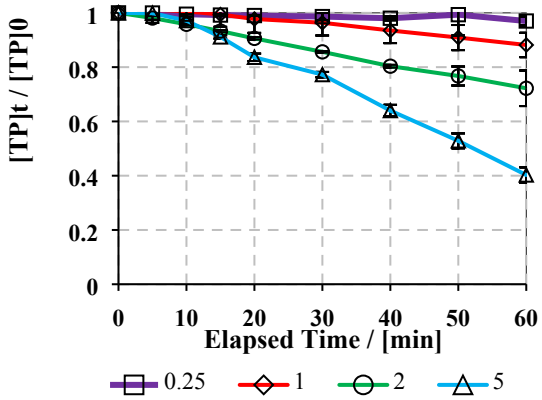


Fig. 4S. Effect of $[PS]_0$ on TP degradation in TAP systems. Experimental conditions: $[TP]_0$ = 10 mg L^{-1}, $[PS]_0$ = 0.25-5 mM and T = 60°C. Error bars are calculated as $\frac{ts}{\sqrt{n}}$, where absent bars fall within the symbols.

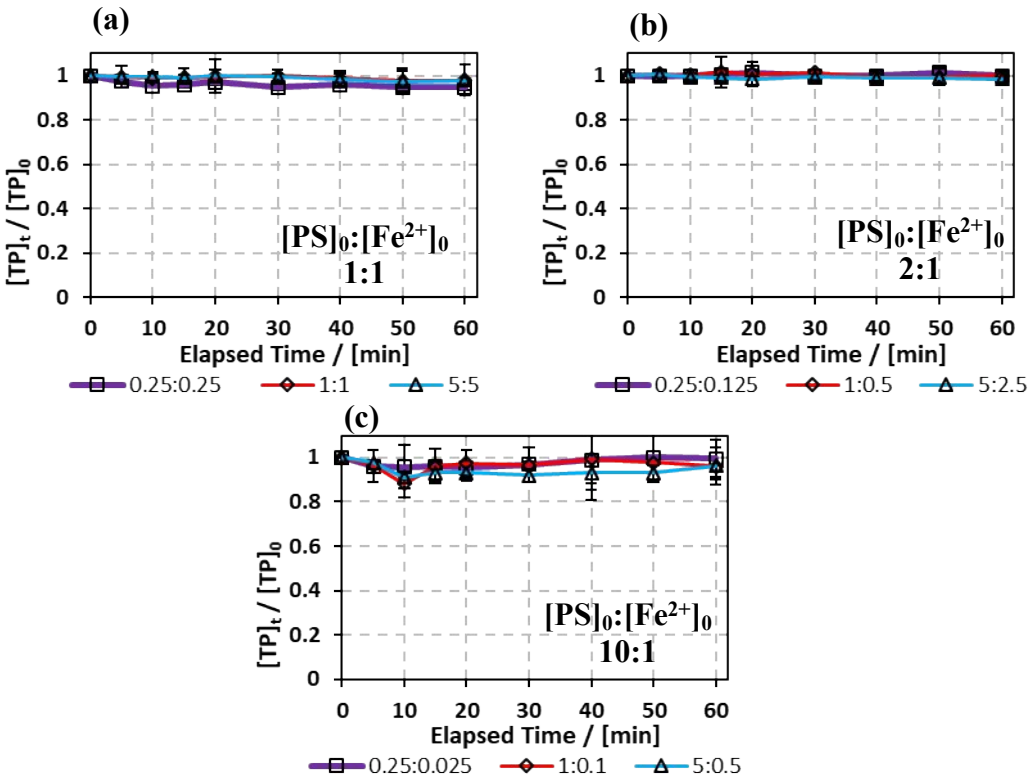


Fig. 5S. Effect of $[PS]_0$:$[Fe^{2+}]_0$ ratio on TP degradation in CAP system. Experimental conditions: $[TP]_0$ = 10 mg L^{-1}, $[PS]_0$ = 0.25, 1 and 5 mM, T = 20°C, and $[PS]_0$:$[Fe^{2+}]_0$ ratio is (a) 1:1 (b) 2:1 and (c) 10:1. Error bars are calculated as $\frac{ts}{\sqrt{n}}$, where absent bars fall within the symbols.

Text S2

Kinetics study in TAP system

Kinetics study was done in TAP system, for T = 55-60°C, $[PS]_0$ = 0.25-5 mM and $[TP]_0$ = 10 mg L^{-1}. Eq. (1) presents the pseudo-first order rate equation, with k_{obs} representing the pseudo-first-order rate constant (min^{-1}), and t representing time (min). Table S1 shows the calculated observed rate constant (k_{obs}) for the different conditions, with the corresponding linearity constant for each plot of $\ln \frac{[TP]}{[TP_0]}$ versus time. The high linearity frequently obtained proves that the reaction follows a pseudo-first order rate. Pseudo-first order kinetics is frequently considered for degradation reactions of organic contaminants by activated PS [2–6].

Table 1S.

TP degradation in TAP system at T = 55-60°C, $[PS]_0$ = 0.25-5 mM and $[TP]_0$ = 10 mg L^{-1} for all studied cases. k_{obs} is calculated for pseudo-first order reaction rate and the corresponding linearity constant (R^2) and reaction half-life ($t_{1/2}$) are presented.

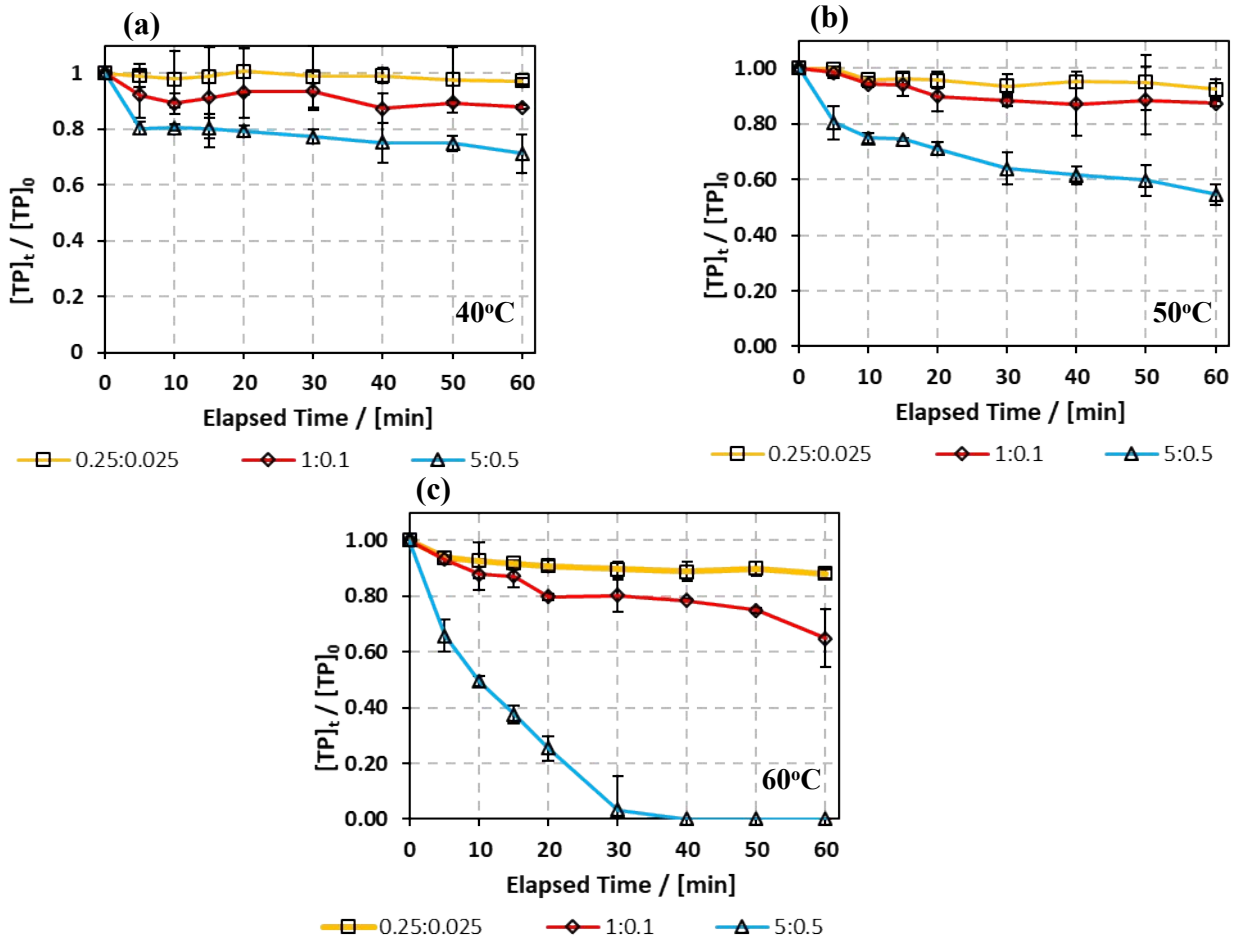
$[TP]_0$ mg L^{-1}	T °C	$[PS]_0$ mM	k_{obs} min^{-1}	R^2	$t_{1/2}$ min
10	55	2	2.63 (±0.04) x 10^{-3}	0.998	263
	60	0.25	3.8 (±0.1) x 10^{-4}	0.680	17 x 10^2
		1	2.2 (±0.1) x 10^{-3}	0.959	30 x 10^1
		2	5.52 (±0.08) x 10^{-3}	0.998	125
		5	1.5 (±0.1) x 10^{-2}	0.956	46
	65	2	1.43 (±0.05) x 10^{-2}	0.988	48.2
	70		4.6 (±0.5) x 10^{-2}	0.928	15
	75		5.3 (±0.7) x 10^{-2}	0.918	13

$$\ln \frac{[TP]}{[TP_0]} = - k_{obs} t \quad (1)$$

Text S3

Kinetics study in TCAP system

Kinetics study was done in TCAP system at $[PS]_0$ = 0.25 - 5 mM, $[PS]_0$:$[Fe^{2+}]_0$ ratio of 1:1, and T = 60°C. Eq. (1) presenting the pseudo-first order rate was fitted. Table 3 shows the calculated observed rate constant (k_{obs}) for the different $[PS]_0$, with the corresponding linearity constant for each plot of $\ln \frac{[TP]}{[TP_0]}$ versus time. The high linearity frequently obtained



proves that the reaction follows a pseudo-first order rate.

Fig. 6S. Effect of temperature on the degradation of TP in TCAP system. Experimental conditions: $[TP]_0$ = 10 mg L^{-1}, $[PS]_0$ = 0.25, 1 and 5 mM, $[PS]_0$:$[Fe^{2+}]_0$ ratio is 10:1, and

temperature is (a) 40°C (b) 50°C and (c) 60°C. Error bars are calculated as $\frac{ts}{\sqrt{n}}$, where absent bars fall within the symbols.

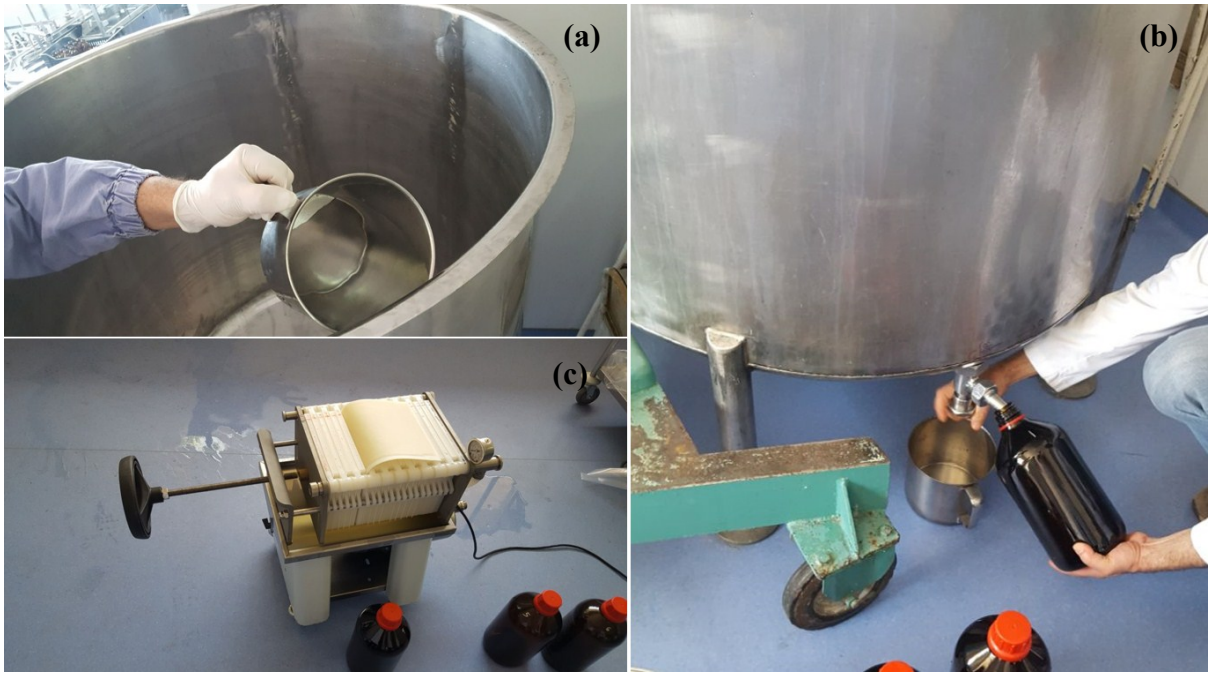


Fig. 7S. Collecting pharmaceutical water effluent. (a) Washing of the 1000 L 316 SS L mixing container, (c) water collected from the container, and (c) the filter press used in the manufacturing process.

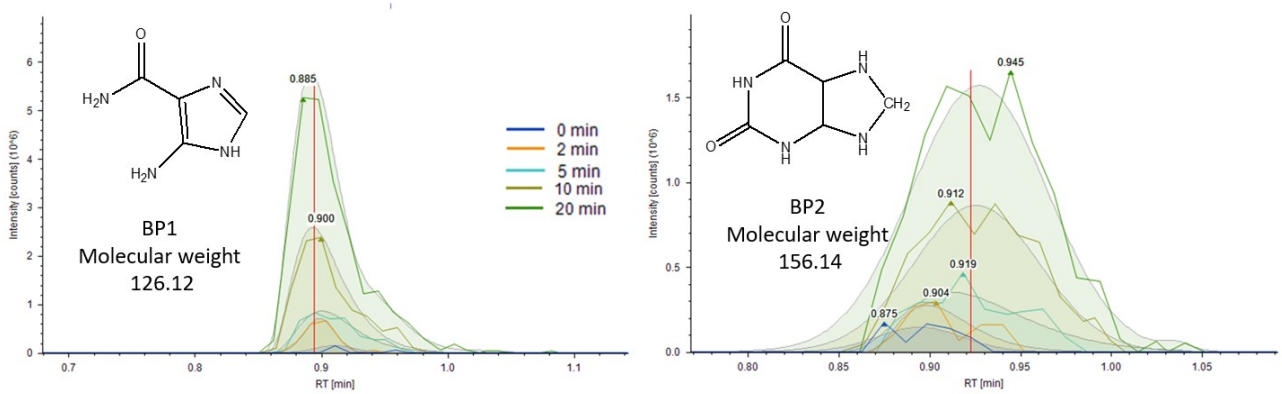


Fig. 8S. Extracted chromatograms of two by-products detected by LC/MS/MS. Intensity of peaks is displayed at reaction time 0 – 20 min.

Table 2S.

Masses and prices of reagents used based on commercial prices where 1 kg of PS costs 2 US $[a], 1 Kg of $FeCl_2.4H_2O$ costs 1.7 US $[b], and 1 L of HCl (37%), used to dissolve the iron salt, costs 0.3 US $[c].

$[PS]_0$ mM	25	50	75	100
$[Fe^{2+}]_0$ mM	25	50	75	100
Reactor volume L	0.2	0.2	0.2	0.2
n PS mol	0.005	0.01	0.015	0.02
n Fe mol	0.005	0.01	0.015	0.02
m $Na_2S_2O_8$ g	1.19	2.38	3.57	4.76
m $FeCl_2.4H_2O$ g	0.994	1.99	2.98	3.98
v HCl (37%) mL	1.25	2.50	3.75	5.00
Total cost \$ $reactor^{-1}$	0.00445	0.00889	0.0133	0.0178
Total cost \$ m^{-3}	22.2	44.5	66.7	88.9

[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.

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