Metabisulfite as an Unconventional Reagent for Green Oxidation of Emerging Contaminants Using an Iron-Based Catalyst

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SUPPORTING INFORMATION

Table S1 reports the degradation percentages in all the conditions investigated with the most significant experimental parameters. Figure S1 reports datasets of kinetic trend obtained from replicate experiments of degradation of phenol using metabisulfite as reagent. Details about the degradation efficiency of the Fe-TAML/hydrogen peroxide system as a function of pH are also reported. Figures S2-S8 report the kinetic trends in the degradation of the different contaminants of emerging concern. Figure S9 reports the values of degradation percentage of contaminants of emerging concern from replicate experiments. Figure S10-S17 report the data obtained from cyclic voltammetry measurements performed with the different contaminants of emerging concern.

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Table S1 Degradation percentage in all the conditions investigated. The most significant experimental parameters are also reported.

Substrate	Substrate concentration, mM	pH	[Fe-TAML®], mM	[reagent], mM	Addition step	[Quencher], mM	% degradation
Phenol	0.1	9	###	$[SO_3^{2-}]$, 0.1	3	###	0
Phenol	0.1	7	0.01	$[SO_3^{2-}]$, 0.1	3	###	49
Phenol	0.1	9	0.01	$[SO_3^{2-}]$, 0.1	3	###	54
Phenol	0.1	11	0.01	$[SO_3^{2-}]$, 0.1	3	###	64
Phenol	0.1	9	###	$[S_2O_5^{2-}]$, 0.1	3	###	3
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	76
Phenol	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	92
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	99
Phenol	0.1	9	###	$[S_2O_8^{2-}]$, 0.1	3	###	1
Phenol	0.1	7	0.01	$[S_2O_8^{2-}]$, 0.1	3	###	0
Phenol	0.1	9	0.01	$[S_2O_8^{2-}]$, 0.1	3	###	3
Phenol	0.1	11	0.01	$[S_2O_8^{2-}]$, 0.1	3	###	0
Phenol	0.1	7	0.01	$[H_2O_2]$, 0.1	3	###	46
Phenol	0.1	9	0.01	$[H_2O_2]$, 0.1	3	###	97
Phenol	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	95
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.3	1	###	49
Phenol	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.3	1	###	53
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.3	1	###	79
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	1	###	36
Phenol	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	1	###	44
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	1	###	47
ACE	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	4
ACE	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	4
ACE	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	1
ACE	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	0
NPX	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	16
NPX	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	17
NPX	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	8
NPX	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	2
IBU	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	9

IBU	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	9
IBU	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	7
IBU	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	4
DCF	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	52
DCF	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	69
DCF	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	95
DCF	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	99
ATZ	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	16
ATZ	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	17
ATZ	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	8
ATZ	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	3
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	82
Phenol	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	99
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	100
Phenol	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	100
BP3	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	80
BP3	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	98
BP3	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	98
BP3	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	99
TCS	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	59
TCS	0.1	9	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	100
TCS	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	100
TCS	0.1	11	0.01	$[H_2O_2]$, 0.1	3	###	100
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	[2-PrOH] = 133	57
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	[t-BuOH] = 40	57
Phenol	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	76
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	[2-PrOH] = 133	90
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	[t-BuOH] = 40	94
Phenol	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	76
BP3	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	[2-PrOH] = 133	65
BP3	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	[t-BuOH] = 40	61
BP3	0.1	7	0.01	$[S_2O_5^{2-}]$, 0.1	3	###	70
BP3	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	[2-PrOH] = 133	63
BP3	0.1	11	0.01	$[S_2O_5^{2-}]$, 0.1	3	[t-BuOH] = 40	86

BP3	0.1	11	0.01	[$S_2O_5^{2-}$], 0.1	3	###	100
BP3	0.1	7	0.01	[H_2O_2], 0.1	3	[2-PrOH] = 133	75
BP3	0.1	7	0.01	[H_2O_2], 0.1	3	[t-BuOH] = 40	74
BP3	0.1	7	0.01	[H_2O_2], 0.1	3	###	70
BP3	0.1	11	0.01	[H_2O_2], 0.1	3	[2-PrOH] = 133	80
BP3	0.1	11	0.01	[H_2O_2], 0.1	3	[t-BuOH] = 40	90
BP3	0.1	11	0.01	[H_2O_2], 0.1	3	###	100
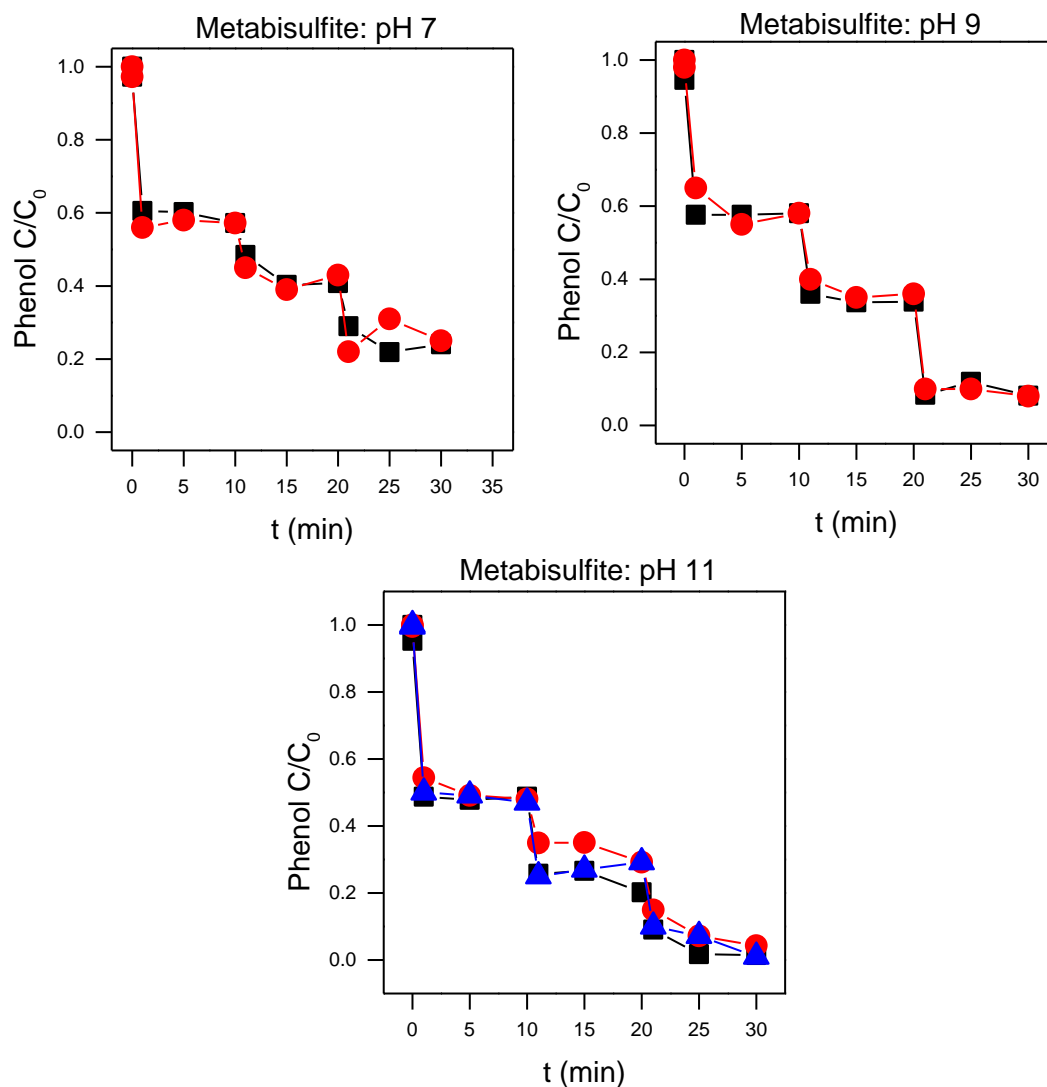
Figure S1. Duplicates and triplicates of kinetics trends in the degradation of phenol using metabisulfite as reagent. All the reactions were carried out by adding an aliquot of 0.1 mM metabisulfite every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®]=0.01 mM; [Contaminant]=0.1 mM.

**Details about the degradation efficiency of the Fe-TAML/hydrogen peroxide system as a function of pH**

$$[FeL(OH_2)_2]^- \leftrightarrows [FeL(OH_2)(OH)]^{-2} + H^+ \qquad K_{a1} \approx 9\text{-}10$$

$$H_2O_2 \leftrightarrows HO_2^- + H^+ \qquad K_{a1} \approx 11.2\text{-}11.6$$

$$[FeL(OH_2)_2]^- + H_2O_2 \xrightarrow{k_1} \text{Oxidized Fe-TAML}$$

$$[FeL(OH_2)(OH)]^{-2} + H_2O_2 \xrightarrow{k_2} \text{Oxidized Fe-TAML}$$

$$[FeL(OH_2)_2]^- + HO_2^- \xrightarrow{k_3} \text{Oxidized Fe-TAML}$$

$$[FeL(OH_2)(OH)]^{-2} + HO_2^- \xrightarrow{k_4} \text{Oxidized Fe-TAML}$$
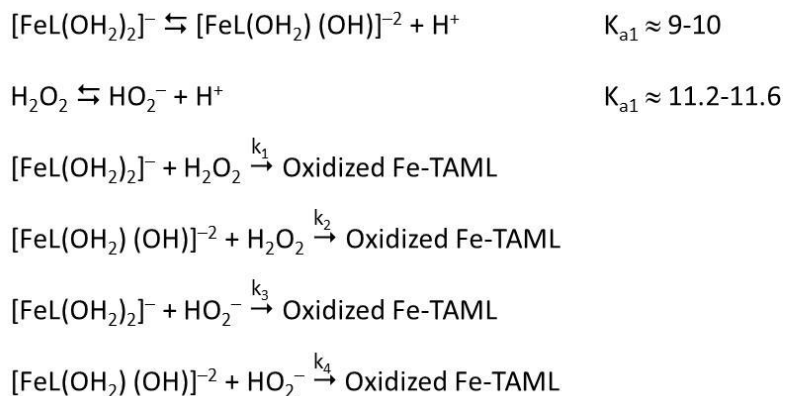
Scheme 1 Reactions involved in the activation of H_2O_2 by Fe-TAML, from Ghosh et al., *J. Am. Chem. Soc.* **2008**, 130, 15116–15126.

The pH profiles in **Figure 3** of the main manuscript are rationalized quantitatively using the known pK_a constants of the catalyst and of H_2O_2. The Fe-TAML activator is almost certainly six coordinate in water with two axial aqua ligands with the first pK_{a1} lying in the range 9-10. The diaqua and aqua/hydroxo Fe^{III} complexes are likely reactive species that interact with either H_2O_2 or its conjugate base ($pK_{a1} \approx 11.2\text{-}11.6$), with the rate constants k_1-k_4 to produce an oxidized Fe-TAML. It is reasonable to assume that neutral H_2O_2 would oxidize a more electron-rich Fe-TAML activator, thus, $k_2 > k_1$. At the same time, it is reasonable to assume that a deprotonated H_2O_2 molecule is a more active binder than the neutral one, thus, $k_3 > k_2$. Also, the interaction with a deprotonated Fe-TAML activator and a deprotonated H_2O_2 molecule is hindered because of Coulombic resistance, thus, $k_3 > k_4$. Based on the abovementioned considerations, it is possible to understand why the maximum of reactivity is at slightly basic pH.
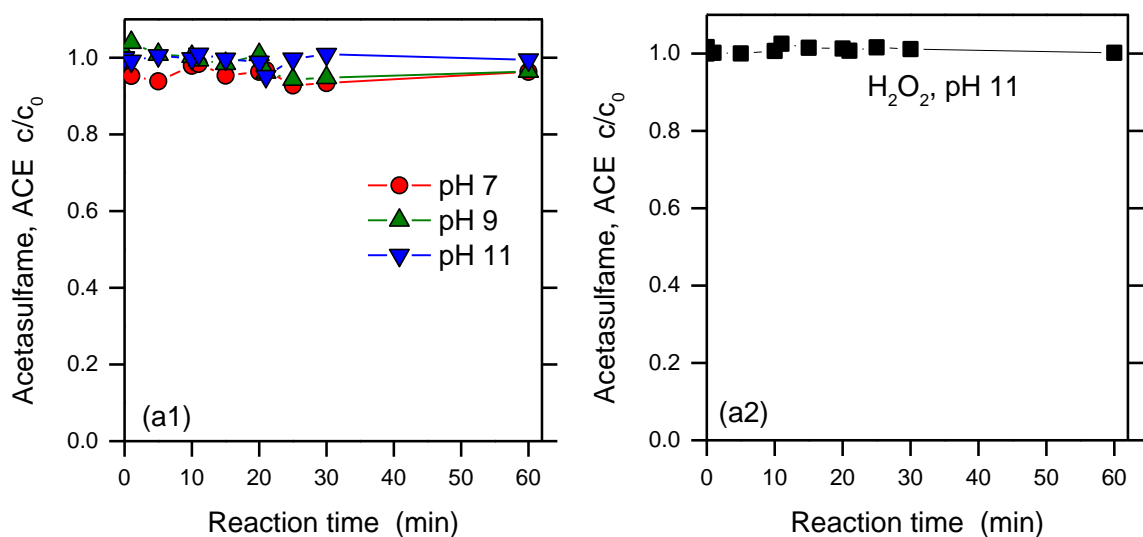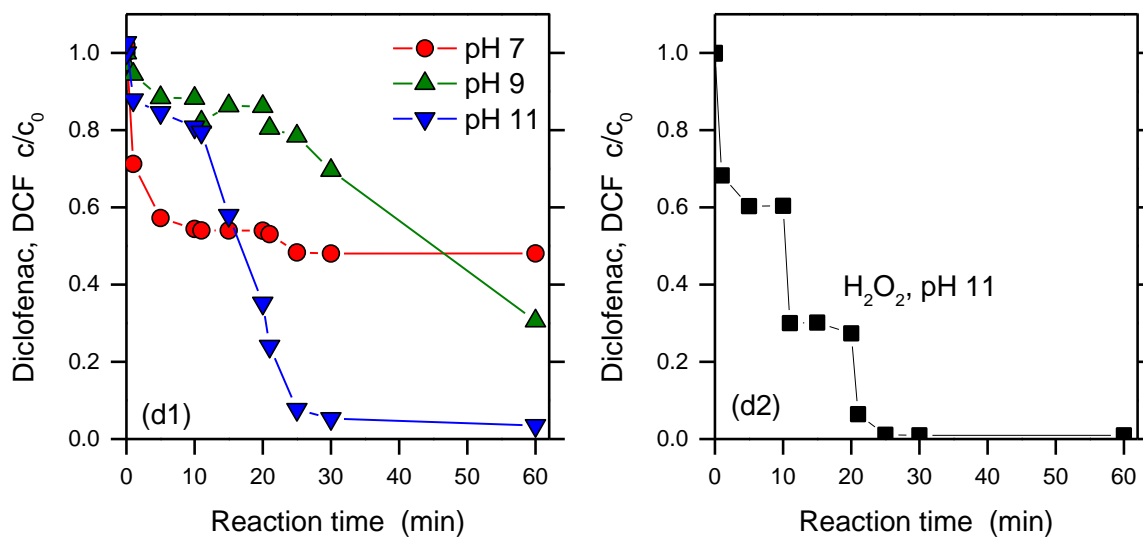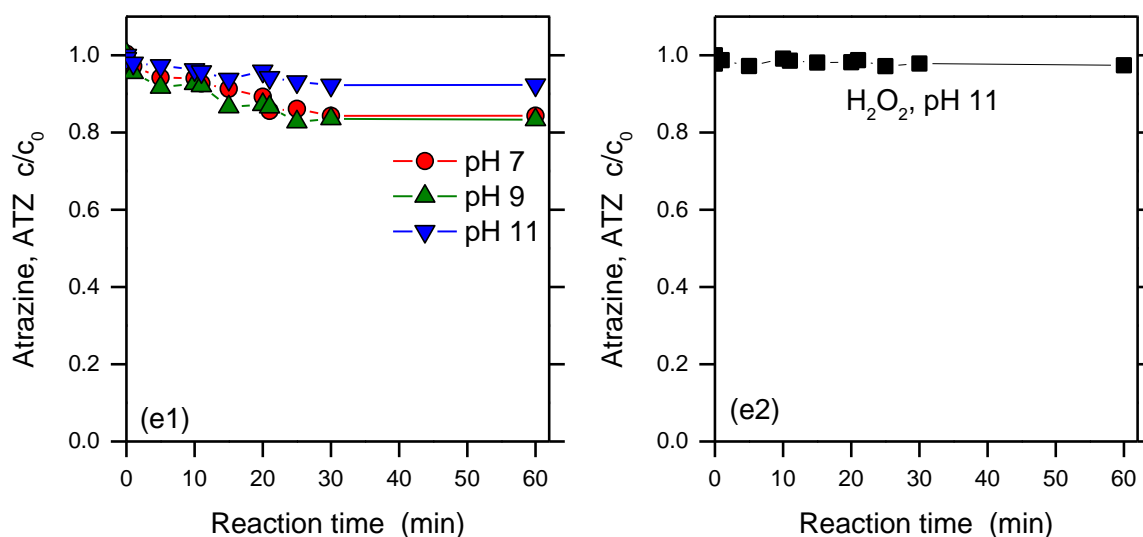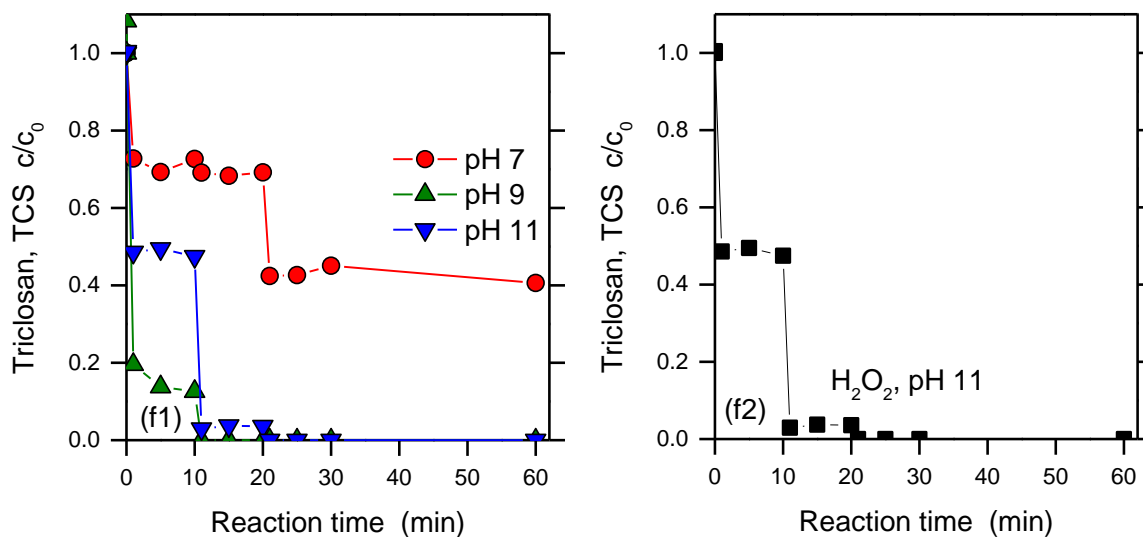
Figure S2 Trends in the degradation of ACE carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (a1) 0.1 mM H_2O_2 (a2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; $[ACE]_0$ = 0.1 mM
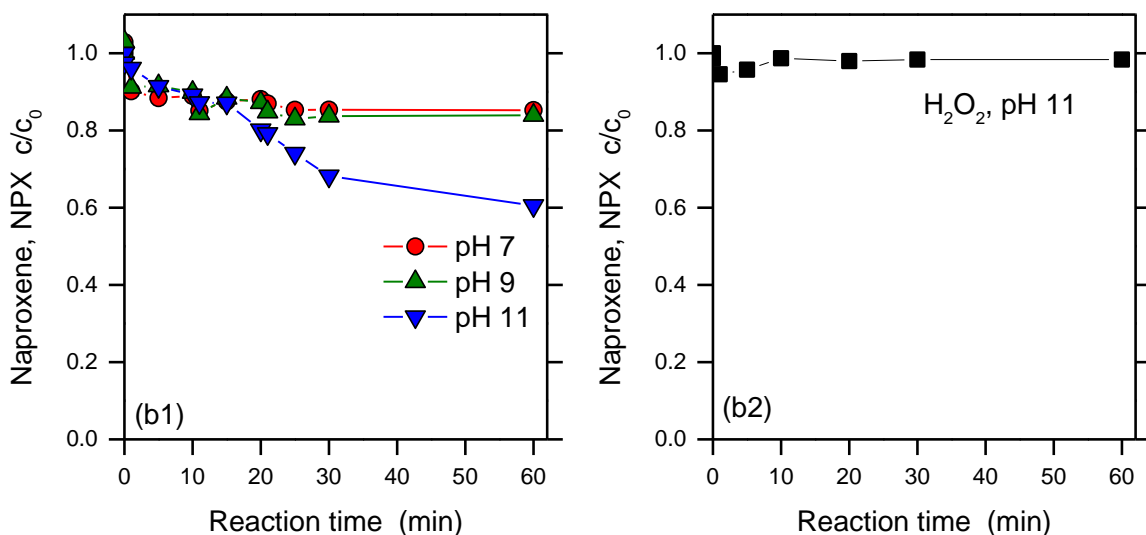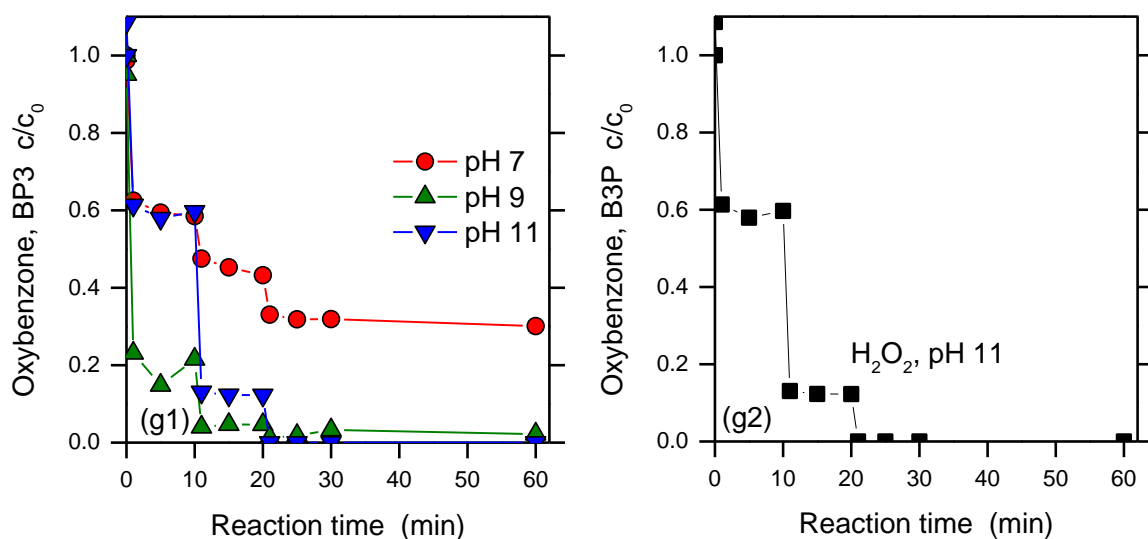

Figure S3 Trends in the degradation of NPX carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (b1) 0.1 mM H_2O_2 (b2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; $[NPX]_0$ = 0.1 mM

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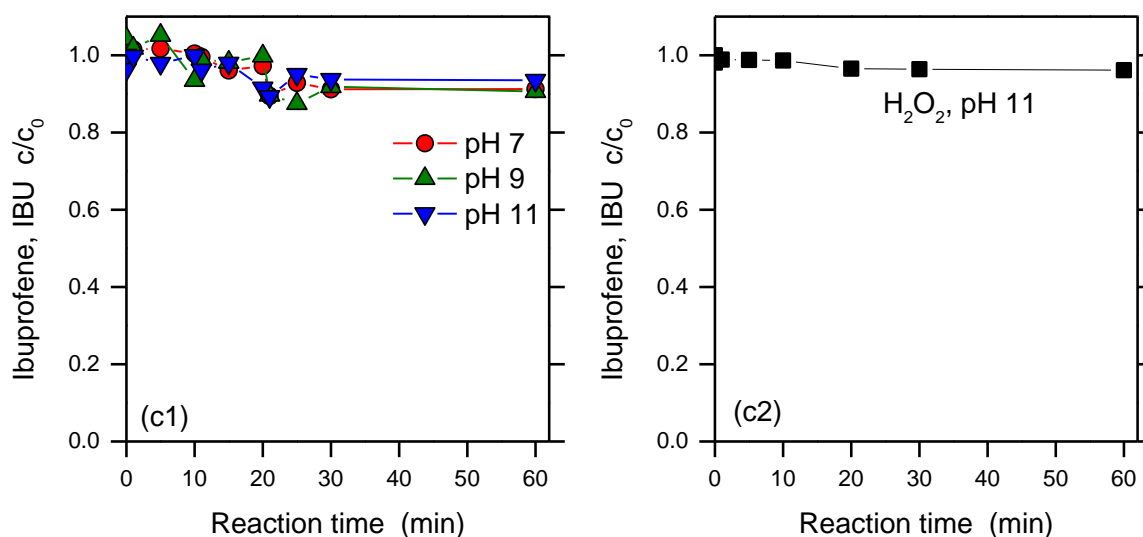
Figure S4 Trends in the degradation of IBU carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (c1) 0.1 mM H_2O_2 (c2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; [IBU]$_0$ = 0.1 mM


Figure S5 Trends in the degradation of DCF carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (d1) 0.1 mM H_2O_2 (d2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; [DCF]$_0$ = 0.1 mM

Figure S6 Trends in the degradation of ATZ carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (e1) 0.1 mM H_2O_2 (e2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; $[ATZ]_0$ = 0.1 mM

Figure S7 Trends in the degradation of TCS carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (f1) 0.1 mM H_2O_2 (f2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; $[TCS]_0$ = 0.1 mM

Figure S8 Trends in the degradation of BP3 carried out by adding an aliquot of 0.1 mM $K_2S_2O_5$ (a1) 0.1 mM H_2O_2 (a2) and reagent every 10 minutes. To perform the reactions at pH 7, 9, or 11, a phosphate buffer solution (10 mM) was used. Initial conditions were: [Fe-TAML®] = 0.01 mM; [BP3]$_0$ = 0.1 mM
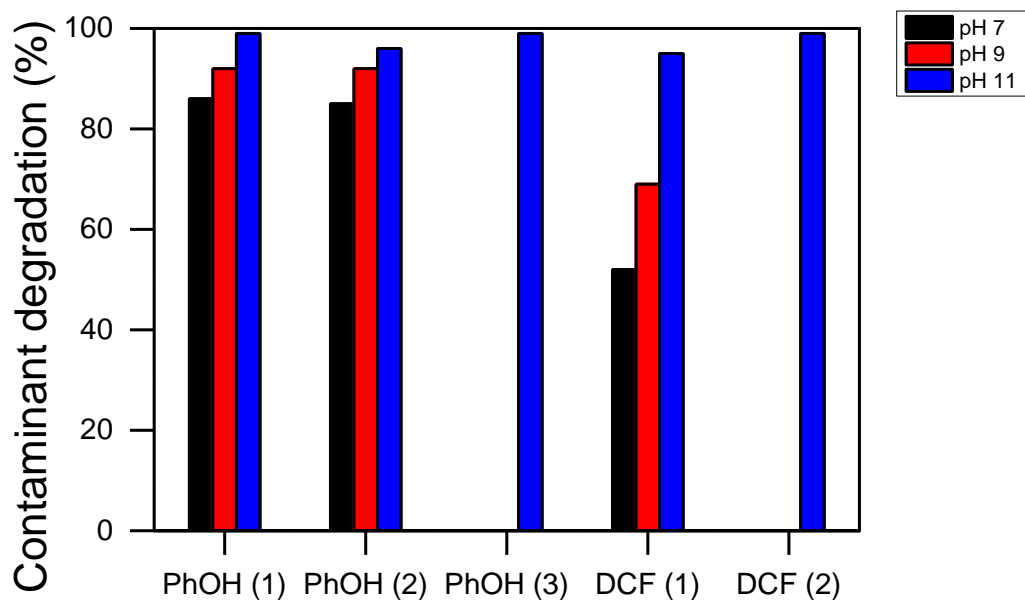
Figure S9. Duplicates and triplicates of tests to measure the degradation % of contaminants of emerging concern. Metabisulfite was used as reagents at different pH values. The reactions were carried out in phosphate buffer (10 mM) by adding 0.1 mM of reagent every 10 minutes for three times (0, 10, 20 min). Initial conditions were [Fe-TAML®] = 0.01 mM; [Contaminant] = 0.1 mM.
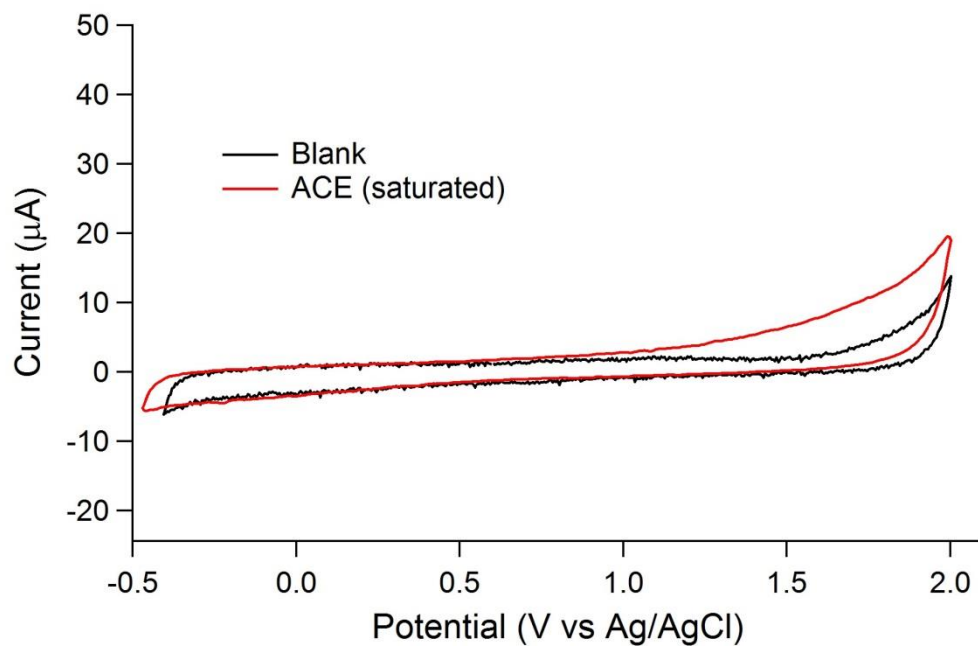
Figure S10. Cyclic voltammetry of saturated acesulfame K (ACE) in 0.1 M $NaClO_4$ in CH_3CN at a scan rate of 100 mV s^{-1}.
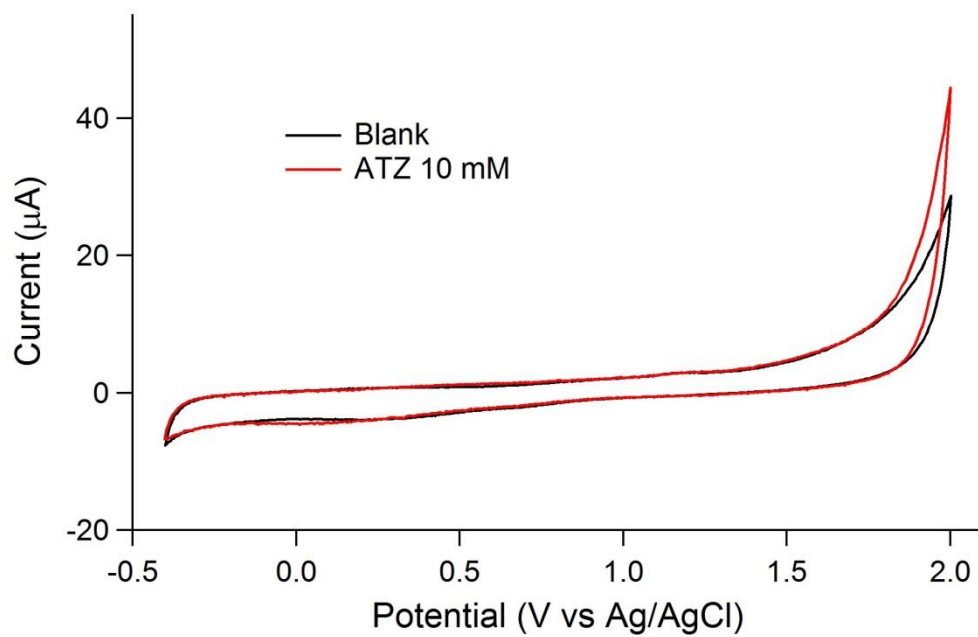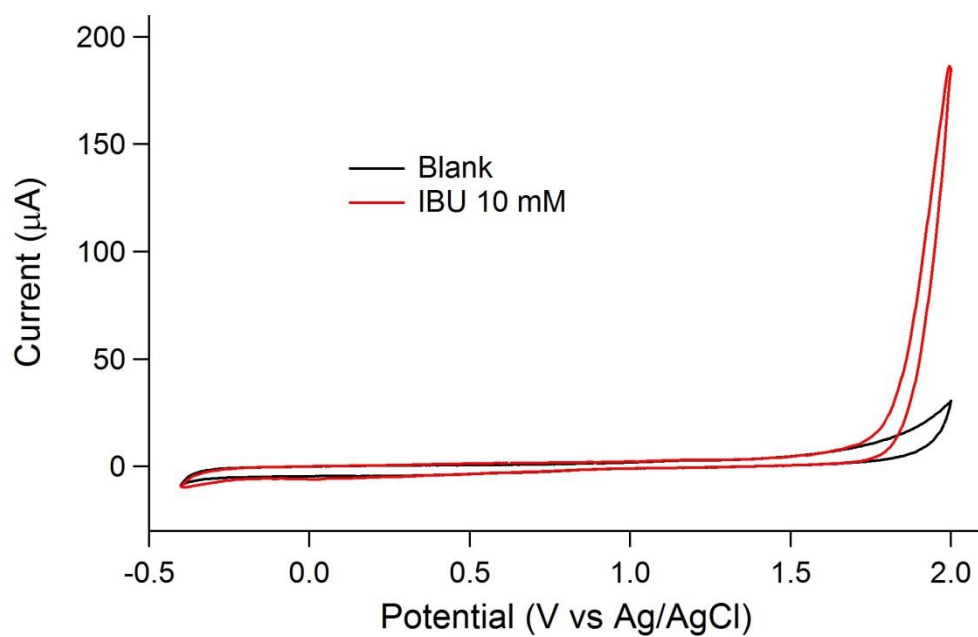

Figure S11. Cyclic voltammetry of saturated atrazine (ATZ) in 0.1 M $NaClO_4$ in CH_3CN at a scan rate of 100 mV s^{-1}.
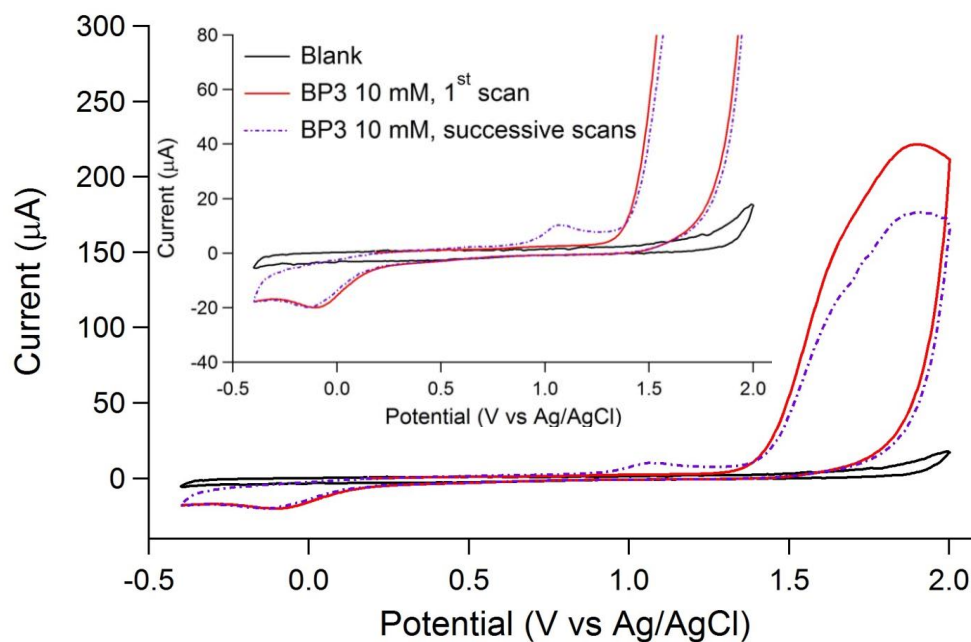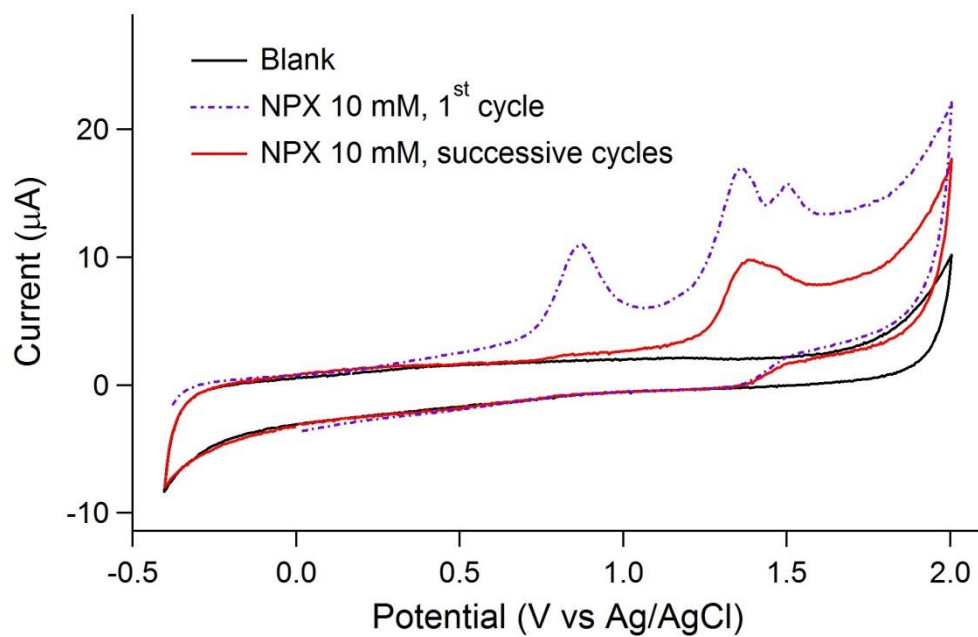
Figure S12. Cyclic voltammetry of 10 mM oxybenzone (BP3) in 0.1 M NaClO$_4$ in CH$_3$CN at a scan rate of 100 mV s^{-1}. The inset represents the magnification of the low current region.
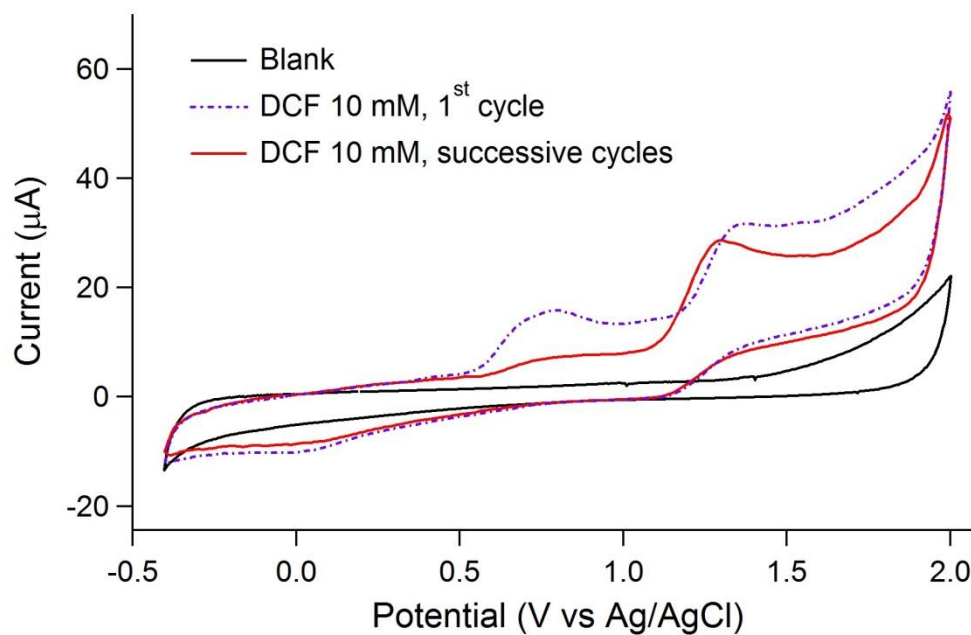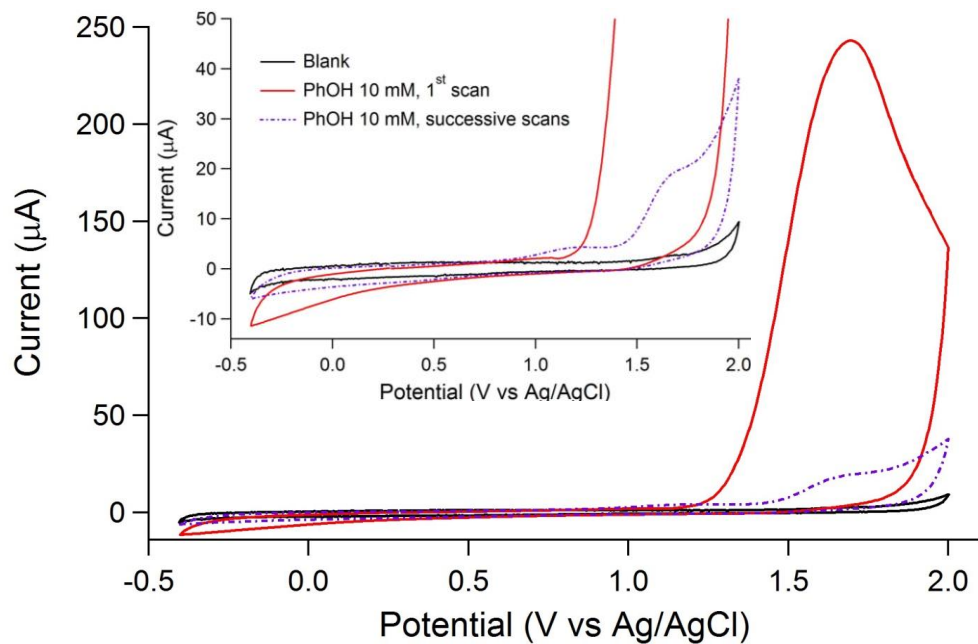

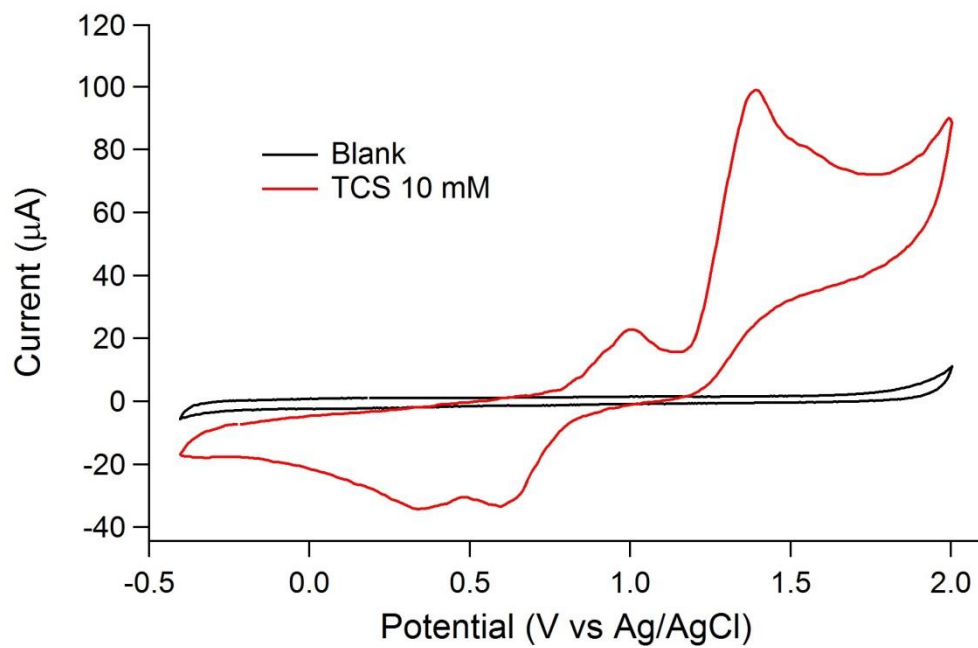**Figure S13.** Cyclic voltammetry of 10 mM diclofenac (DCF) in 0.1 M NaClO$_4$ in CH$_3$CN at a scan rate of 100 mV s^{-1}.

Figure S14. Cyclic voltammetry of 10 mM ibuprofen (IBU) in 0.1 M NaClO$_4$ in CH$_3$CN at a scan rate of 100 mV s^{-1}.

Figure S15. Cyclic voltammetry of 10 mM naproxen (NPX) in 0.1 M NaClO$_4$ in CH$_3$CN at a scan rate of 100 mV s^{-1}.

Figure S16. Cyclic voltammetry of 10 mM phenol (PhOH) in 0.1 M NaClO$_4$ in CH$_3$CN at a scan rate of 100 mV s^{-1}. The inset highlights the behaviour at lower current ranges.

Figure S17. Cyclic voltammetry of 10 mM triclosan (TCS) in 0.1 M NaClO$_4$ in CH$_3$CN at a scan rate of 100 mV s^{-1}.