Supplementary Material

Magnetite-Based Catalyst in the Catalytic Wet Peroxide Oxidation for Different Aqueous Matrices Spiked with Naproxen–Diclofenac Mixture

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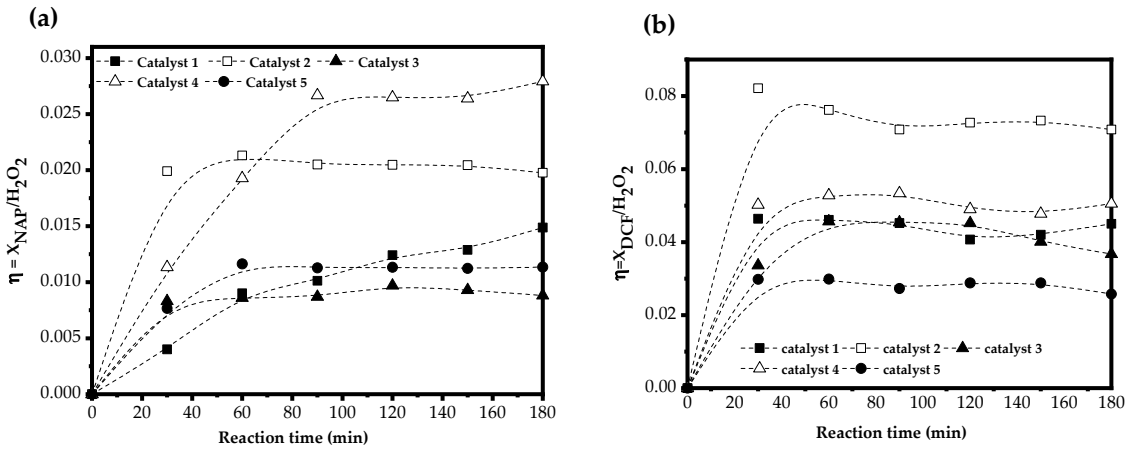


Figure 1. Hydrogen peroxide efficiencies on **(a)** NAP and **(b)** DCF degradation using the different catalyst. Reaction conditions: $[NAP]_0 = [DCF]_0 = 5.0$ mg/L, [catalyst] = 1.0 g/L, pH = 6.3, 1.5 mM H_2O_2 and 70°C. Atmospheric pressure and 3 h of reaction time.

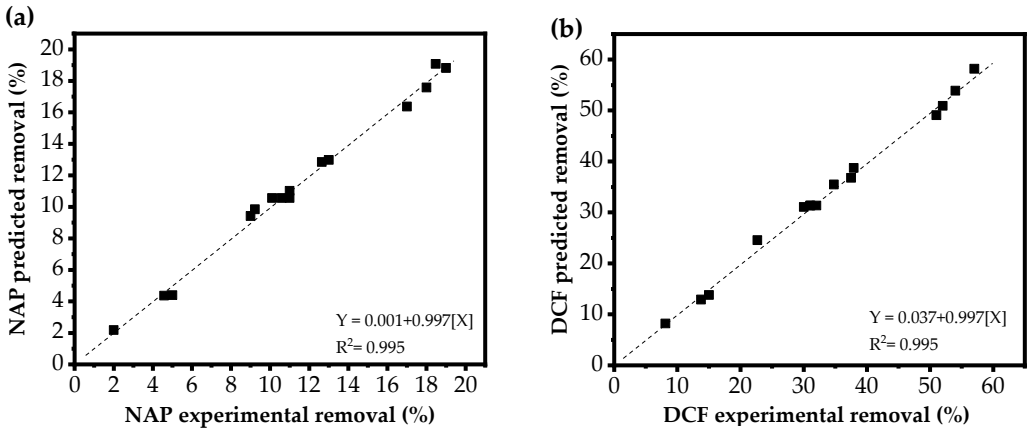


Figure S2. Linear correlation between the experimental and the predicted values of **(a)** NAP and **(b)** DCF removal efficiency. Reaction conditions: $[NAP]_0 = [DCF]_0 = 5.0$ mg/L, [catalyst] = 1.0 g/L. Atmospheric pressure and 3 h of reaction time.

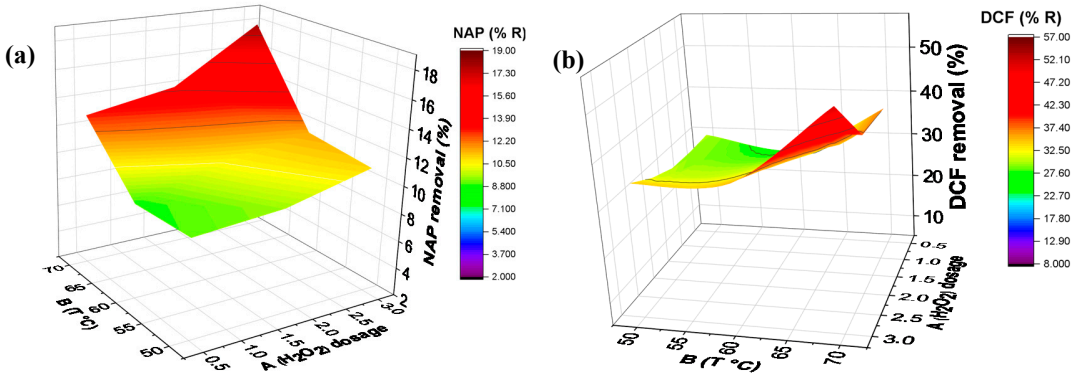


Figure S3. Combined effect of temperature and H_2O_2 on the removal of **(a)** NAP and **(b)** DCF. Reaction conditions: $[NAP]_0 = [DCF]_0 = 5.0$ mg/L, [catalyst] = 1.0 g/L, and atmospheric pressure and 3 h of reaction time.

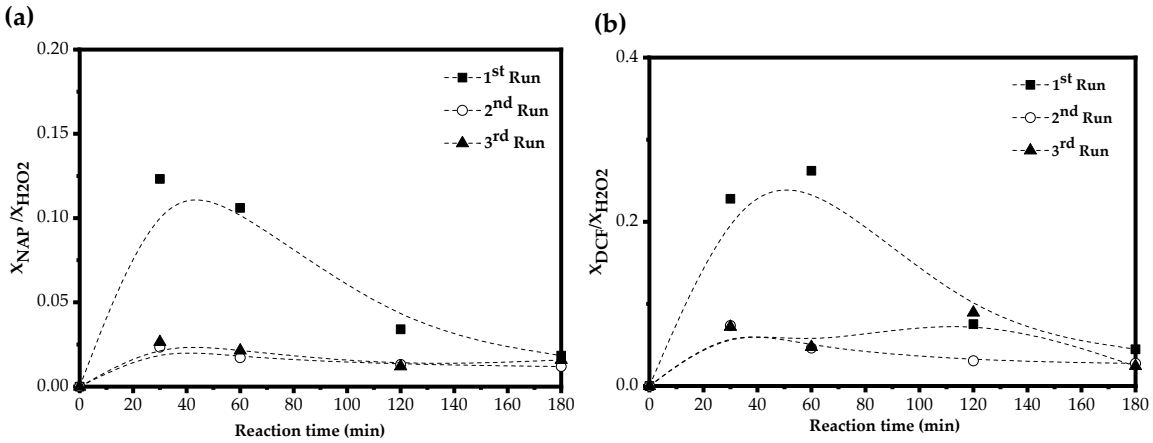


Figure S4. Hydrogen peroxide efficiencies on NAP and DCF degradation at optimal conditions. Reaction conditions: $[NAP]_0 = [DCF]_0 = 5.0$ mg/L, [catalyst] = 1.0 g/L, pH = 6.5, 3 mM H_2O_2 and 50°C. Atmospheric pressure and 3 h of reaction time.

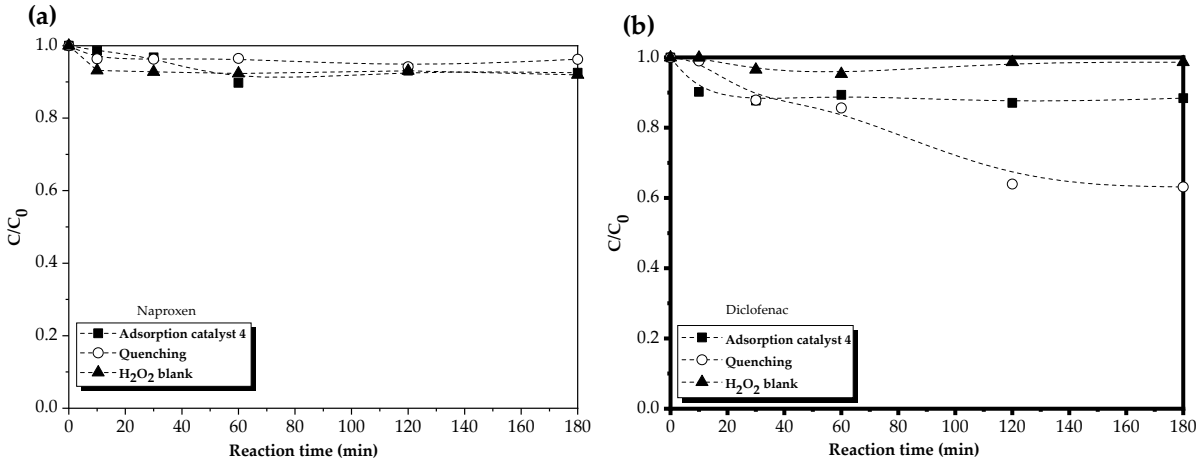
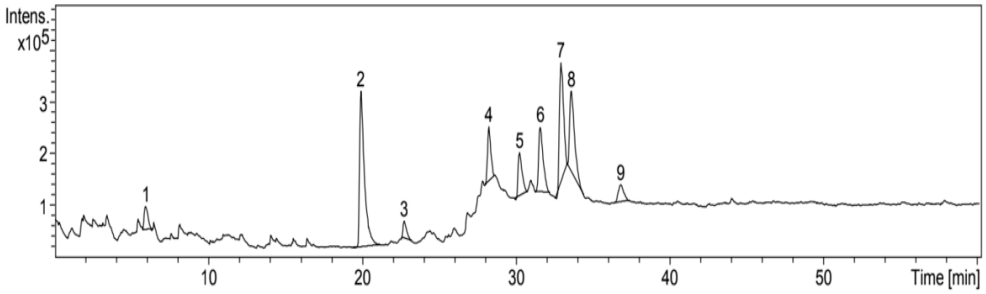
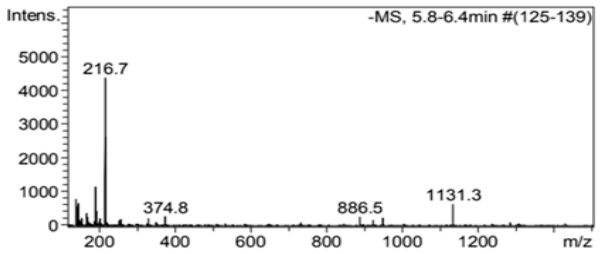


Figure S5. Adsorption blank with the catalyst 4, H_2O_2 blank and quenching test of CWPO for a) NAP and b) DCF. Operating conditions: $[NAP]_0 = [DCF]_0 = 5.0$ mg/L, [catalyst] = 1.0 g/L, pH = 6.5, 3 mM H_2O_2 and 50°C. Atmospheric pressure and 3 h of reaction time.



#	RT [min]	Area
1	6.0	761796
2	19.9	6428387
3	22.7	501605
4	28.2	1542457
5	30.2	1449424
6	31.6	2508016
7	32.9	4235150
8	33.6	3452451
9	36.8	786092

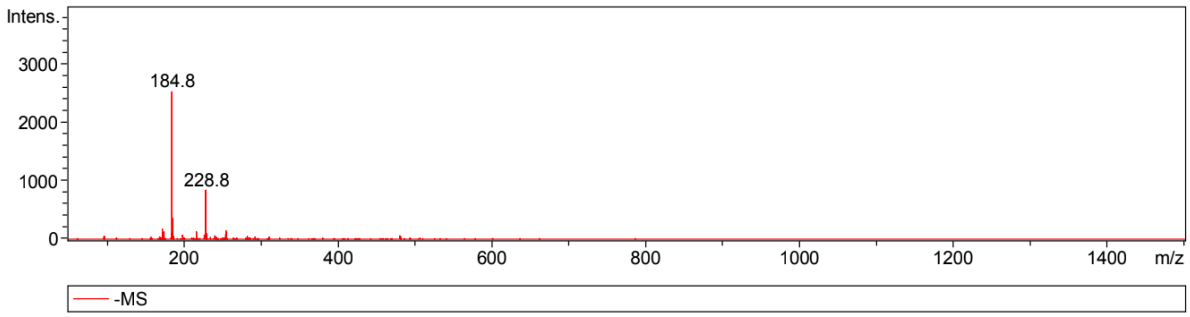
Cmpd 1, 6.0 min



#	m/z	I
1	140.8	782
2	144.6	569
3	146.6	650
4	148.6	198
5	154.7	219
6	168.7	368
7	170.7	250
8	188.8	108
9	189.8	124
10	192.7	1140
11	194.7	420
12	202.6	140
13	204.6	209
14	216.7	4364
15	217.7	287
16	254.5	142
17	256.5	178
18	258.5	186
19	330.4	207
20	350.7	102
21	374.8	260
22	886.5	243
23	922.1	152
24	947.2	193
25	947.5	223
26	1131.3	627

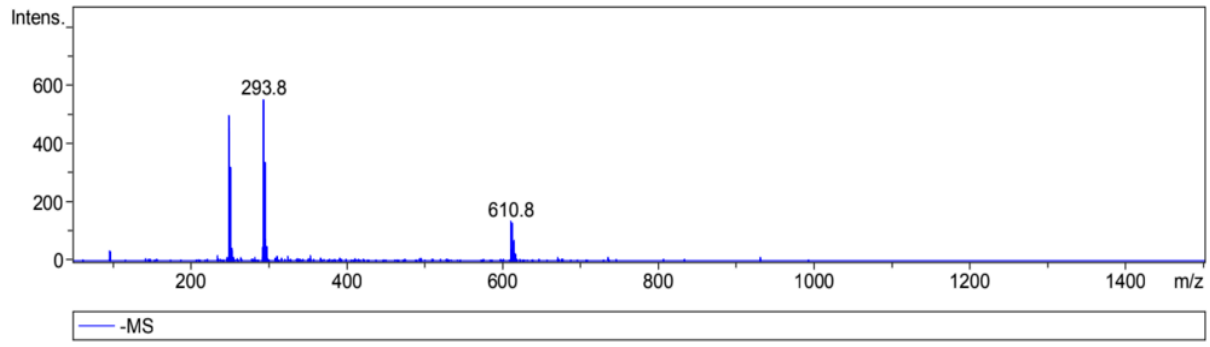
Figure S6. Intermediaries' peaks between NAP (12) and DCF (16) identified in the treated CWPO sample. Reaction conditions: $[NAP]_0 = [DCF]_0 = 5.0$ mg/L, [catalyst4] = 1.0 g/L, pH = 6.5, 3 mM H_2O_2 and 50°C. Atmospheric pressure and 3 h of reaction time.

(a)



#	m/z	I
1	172.9	172
2	174.8	126
3	184.8	2523
4	185.9	358
5	216.8	124
6	228.8	839
7	255.0	143

(b)



#	m/z	I
1	249.8	496
2	251.8	319
3	293.8	551
4	295.8	336
5	610.8	134
6	612.8	128

Figure S7. Characteristic peaks of the a) NAP and b) DCF Standards

Table S1. *p*-test significance of model terms in the NAP quadratic polynomial model.

Model	Model coefficient	Coefficient estimate	Standard error	T Stat	P Value	Degree of significance
Intercept	β_0	10.57	0.40	26.20	<0.00	Significant
A	β_1	1.55	0.25	6.28	0.002	Significant
B	β_2	2.53	0.25	10.23	<0.00	Significant
C	β_3	-5.79	0.25	-23.44	<0.00	Significant
A^2	β_{11}	0.27	0.36	-0.76	0.483	Not significant
B^2	β_{22}	1.91	0.36	5.25	0.003	Significant
C^2	β_{33}	-0.67	0.36	-1.84	0.125	Not significant
AB	β_{12}	0.75	0.35	2.15	0.084	Significant
AC	β_{13}	-1.56	0.35	-4.47	0.007	Significant
BC	β_{23}	1.30	0.35	3.73	0.013	Significant

Table S2. *p*-test significance of model terms in DCF quadratic polynomial model.

Model	Model coefficient	Coefficient estimate	Standard error	T Stat	P Value	Degree of significance
Intercept	β_0	31.37	1.018	30.96	<0.00	Significant
A	β_1	4.63	0.62	7.47	0.001	Significant
B	β_2	5.28	0.62	8.51	<0.00	Significant
C	β_3	-17.55	0.62	-28.29	<0.00	Significant
A^2	β_{11}	2.09	0.91	2.28	0.071	Significant
B^2	β_{22}	5.12	0.91	5.60	0.003	Significant
C^2	β_{33}	-2.54	0.91	-2.78	0.039	Significant
AB	β_{12}	2.43	0.87	2.77	0.039	Significant
AC	β_{13}	-5.08	0.87	-5.79	0.002	Significant
BC	β_{23}	2.89	0.87	3.29	0.022	Significant

Table S3. Intermediates compounds of NAP decomposition in catalytic wet peroxide oxidation with Fe_3O_4/MWCNTs.

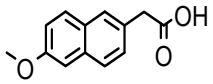
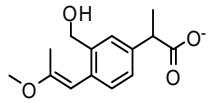
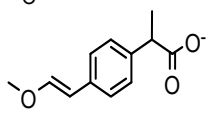
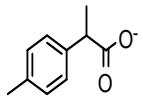
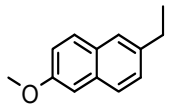
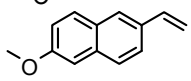
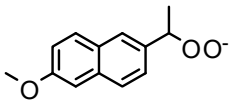
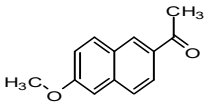
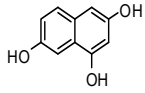
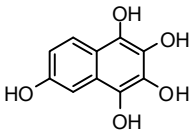
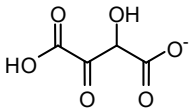
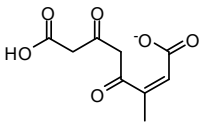
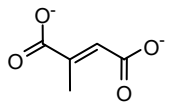
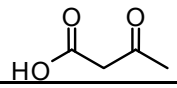
Ion m/z detected by ESI-ms	Molecular weight	w/z (negative)	Chemical structure
C1($C_{14}H_{13}O_3$)-	230	228.8	
C2 ($C_{14}H_{17}O_4$)-	251	249.8[1]	
C3 ($C_{12}H_{13}O_3$)-	206	204.6[1]	
C4 ($C_9H_9O_2$)-	151	149.8[1]	
C5 ($C_{13}H_{15}O$)-	186	186.8	
C6 ($C_{13}H_{13}O$)-	184	184.9	
C7 ($C_{13}H_{13}O_3$)-	218	216.7	
C8 ($C_{13}H_{13}O_2$)-	200	200.9	
C9 ($C_{10}H_7O_3$)-	176	175	
C10 ($C_{10}H_7O_5$)-	208	207	
C11 ($C_4H_3O_6$)-	148	147	
C12 ($C_9H_{10}O_6^-$)	214	213	
C13 ($C_5H_4O_4$)-	130	128.9	
C14 ($C_4H_6O_3$)	102	101	

Table S4. Intermediates compounds of DCF degradation in catalytic wet peroxide oxidation with Fe_3O_4/MWCNTs.

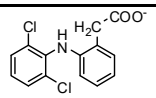
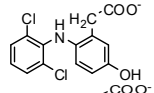
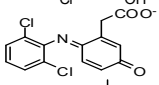
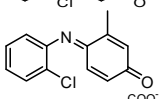
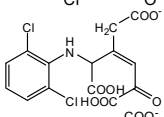
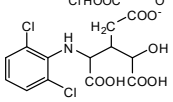
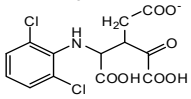
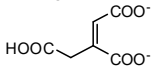
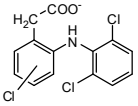
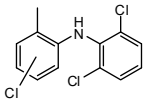
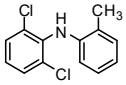
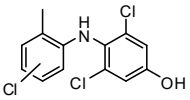
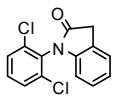
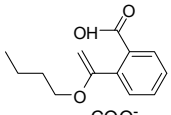
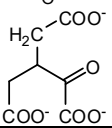
Ion m/z detected by ESI-ms	Molecular weight	w/z (negative)	Chemical structure
C1 ($C_{14}H_{10}NCl_2O_2$)-	295	293.8	
C2 ($C_{14}H_{10}NCl_2O_3$)-	311.9	311	
C3 ($C_{14}H_9NCl_2O_3$)-	310	309	
C4 ($C_{13}H_9ClNO$)-	230.6	229.8	
C5 ($C_{14}H_{10}NCl_2O_7$)-	376	375	
C6 ($C_{13}H_{10}NCl_2O_7$)-	366	364	
C7 ($C_{13}H_8NCl_2O_7$)-	364	362	
C8 ($C_6H_7O_6$)-	175	172.9	
C9 ($C_{14}H_{10}Cl_3N\ O_2$)-	330	329.1	
C10 ($C_{13}H_8Cl_3N$)-	286	284	
C11 ($C_{13}H_{10}NCl_2$)-	251	249.8	
C12 ($C_{13}H_{10}Cl_3NO$)-	301	299.1	
C13 ($C_6H_4NCl_2$)-	162	160.8	
C14 ($C_{14}H_9Cl_2NO$)-	278.13	277	
C15 ($C_{12}H_{14}O_4$)-	222.24	220.8	
C16 ($C_7H_8O_7$)	204	201	

Table S5. Representative analysis of the three real aqueous matrices.

	Hospital water	**Surface water**	**WWTP effluent**
pH	8.6	6.1	9.4
Conductivity (mS/cm²)	1.17	0.1641	0.557
TOC (mg/L)	80	6.8	9.8
Suspended solids (mg/L)	138	140	80
Aromaticity (a.u)	0.50	0.16	0.12
TN (mg/L)	94	0.98	0.87

Table S6. Microbiological counts of the three real aqueous matrices and their CWPO effluents.

Microbiological counts (Log CFU/mL)								
1	**Real aqueous Matrix**	**Enterococcus spp.**	**Total coliforms**	**Escherichia coli**	**Clostridium perfringens**	**Aerobic mesophilic**	**Molds and yeasts**	**Pseudomonas aeruginosa**
2	SW	ND	ND	ND	2.00±0.08	5.44±0.13	3.90±0.03	ND
3	WWTP	ND	ND	ND	2.48±0.08	5.15±0.05	ND	ND
4	HW	5.23±0.51	ND	ND	1.85±0.02	5.45±0.15	5.57±0.11	ND
5	SW-NAP-DCF	ND	ND	ND	2.48±0.14	4.77±0.05	ND	ND
6	WWTP-NAP-DCF	ND	ND	ND	2.48±0.04	1.00±0.01	ND	ND
7	HW-NAP-DCF	2.76±0.06	1.10±0.02	ND	1.30±0.03	5.46±0.09	ND	ND
8	CWPO Effluent of SW after 3h	ND	ND	ND	1.30±0.09	1.48±0.02	4.60±0.05	ND
9	CWPO Effluent of WWTP after 3h	ND	ND	ND	1.48±0.05	2.00±0.04	ND	ND
10	CWPO Effluent of HW after 3h	ND	ND	ND	1.30	ND	ND	ND
11	CWPO Effluent of SW-NAP-DCF after 8h	1.48±0.03	ND	ND	2.78±0.09	3.83±0.06	3.51±0.07	ND
12	CWPO Effluent of WWTP-NAP-DCF after 8h	ND	ND	ND	ND	ND	ND	ND
13	CWPO Effluent of HW-NAP-DCF after 8h	ND	ND	ND	ND	ND	ND	ND