Insight in natural media remediation through ecotoxicity correlation to clay catalyst selectivity in organic molecule ozonation

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SUPPORTING INFORMATION

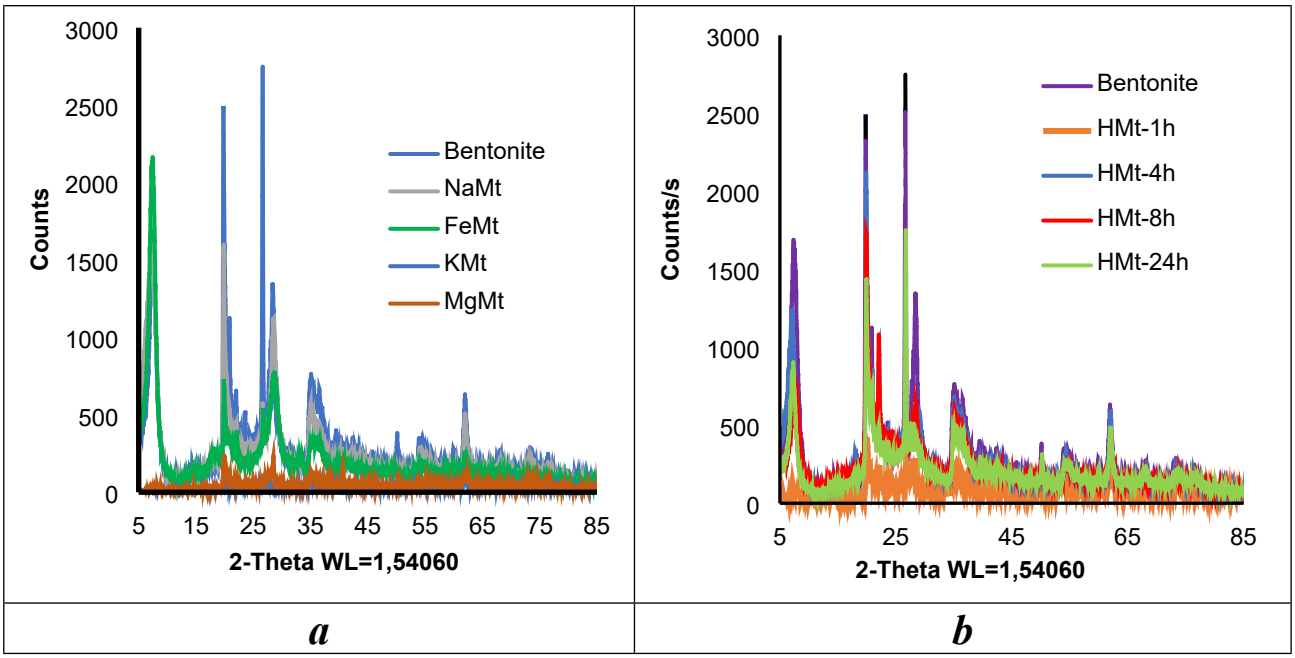
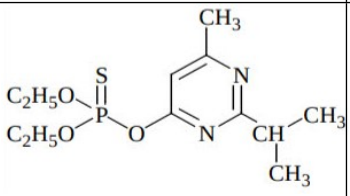
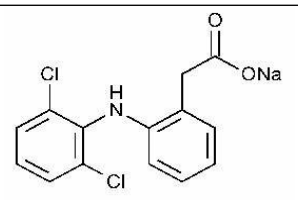


Fig. S1. XRD patterns of ion-exchanged montmorillonites (a) and acid-activated bentonites (b).

Table S1. Some features of the investigated organic molecules.

Organic compound	Structure de la molécule	Oxygen/Carbon atom ratio	pK_a	λ_{max} (nm)	Masse molaire (g/mol)
Diazinon (DAZ)		3/12	2.6	250	304.35
Diclofenac sodium (DCF)		1/14	4.35 ± 0.2	275	318.1

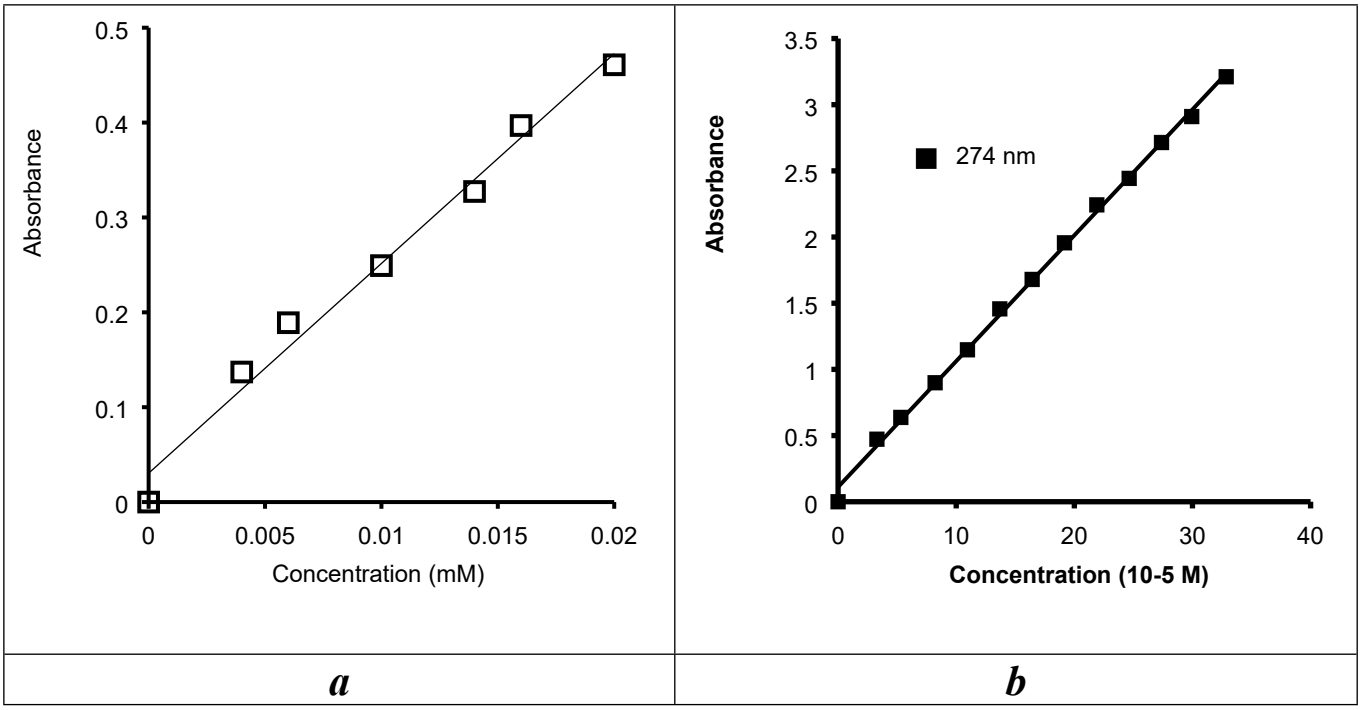


Fig. S2. Calibration curve of DAZ (a) and DCF (b) as assessed by UV-VIS. Quartz cell width: 1 cm.

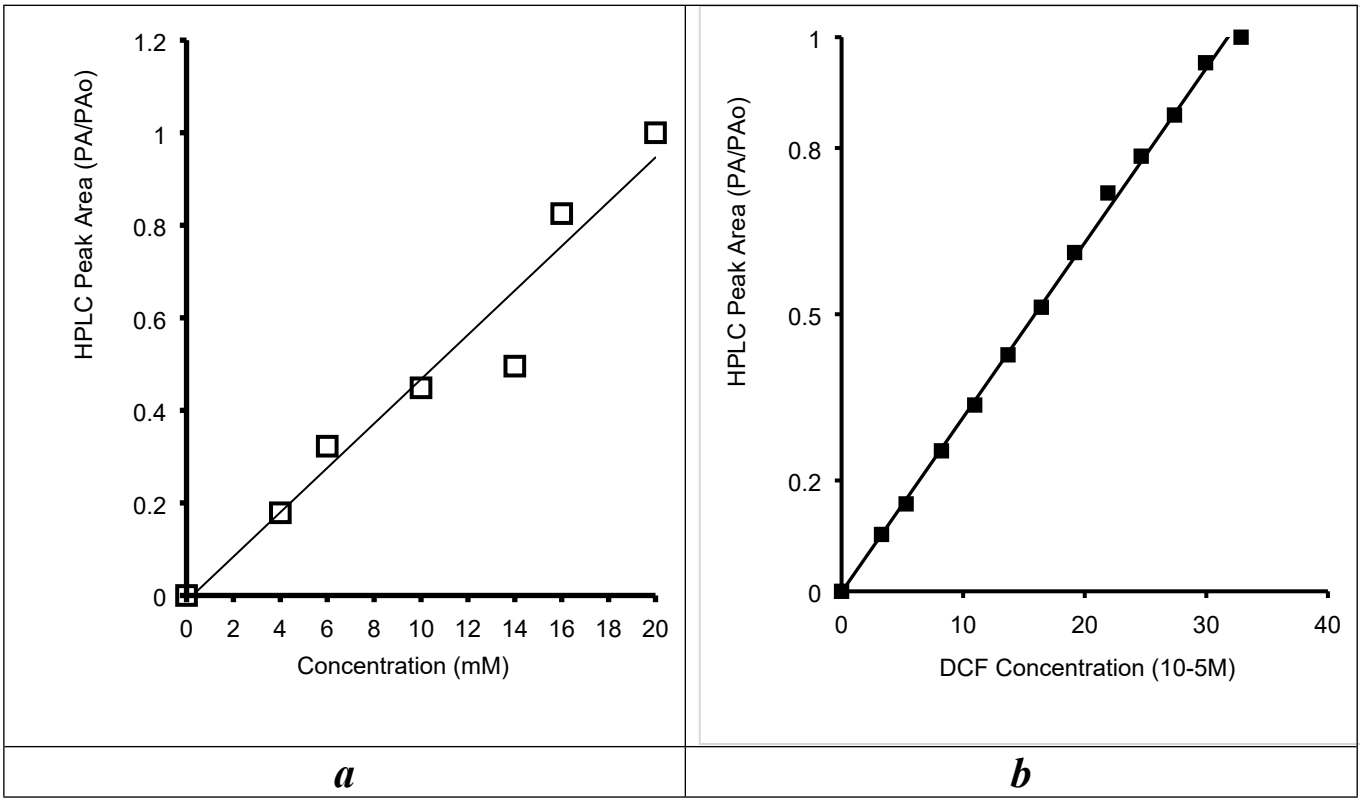


Fig. S3. Calibration curves of DAZ (a) and DCF (b) as assessed by HPLC-UV.

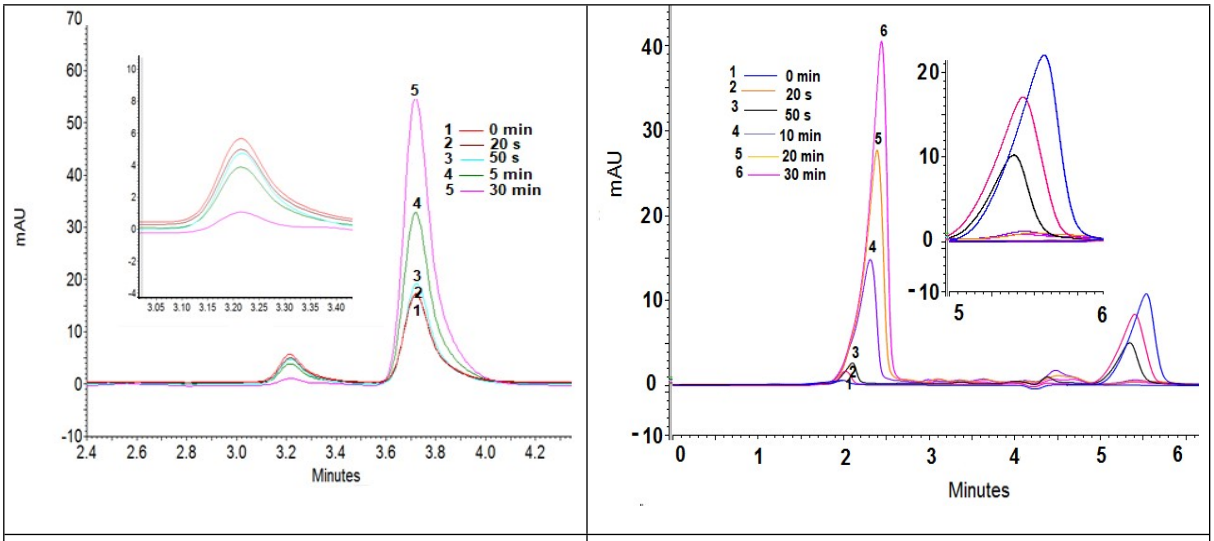


Fig. S4. Evolution during non-catalytic ozonation of the HPLC-UV peak area of Diazinon (a), Diclofenac (b). Ozone flow rate: 600 mg h^{-1}. Sample volume = 20 mL. Substrate initial concentration: 10^{-5} M.

Table S2. Initial physico-chemical feature of the reaction mixture before ozonation.

	Water			DCF		
Catalyst	pH[a]	Particle size (µm)[b]	Zeta potential (mV)[c]	pH[d]	Particle size (µm)[e]	Zeta potential (mV)[f]
Bentonite	6.00	1.50	-21.98	5.60	0.36	-39.58
HMt-1	4.88	1.74	-16.18	4.83	2.07	-34.99
HMt-4	4.50	1.46	-19.38	4.71	1.60	-32.68
HMt-8	4.27	1.74	-34.40	4.63	0.88	-31.25
HMt-15	3.79	1.62	-35.93	4.72	1.37	-27.44
HMt-24	4.25	2.37	-22.29	4.73	2.00	-29.80
NaMt	6.27	0.76	-22.39	4.61	1.07	-30.26
KMt	5.22	0.56	-18.91	5.30	2.10	-33.39
CaMt	4.75	0.67	-23.14	5.01	0.55	-15.49
MgMt	5.80	1.02	-15.85	5.05	0.66	-19.73
CoMt	5.22	1.24	-15.66	5.44	1.32	-18.45
CuMt	4.32	1.99	-05.18	4.59	1.86	-23.63
NiMt	4.54	1.66	-27.22	5.51	1.22	-23.00
Fe(II)Mt	3.76	2.59	-22.20	4.53	2.17	-26.81
LDH	3.94	6.76	+5.54	6.74	3.85	+8.90

a These pH measurements were carried out in 20 mL of distilled water with 40 mg of clay catalyst at T = 22 ° C.
b These particle size values were measured in the absence of organic molecules.
c These Zeta potential values were measured in the absence of organic molecules.
d pH of the aqueous solution in the presence of the organic molecule at T = 22 ° C after addition of catalyst.
e These particle size values were measured in the presence of organic molecules.
f These Zeta potential values were measured in the presence of organic molecules.

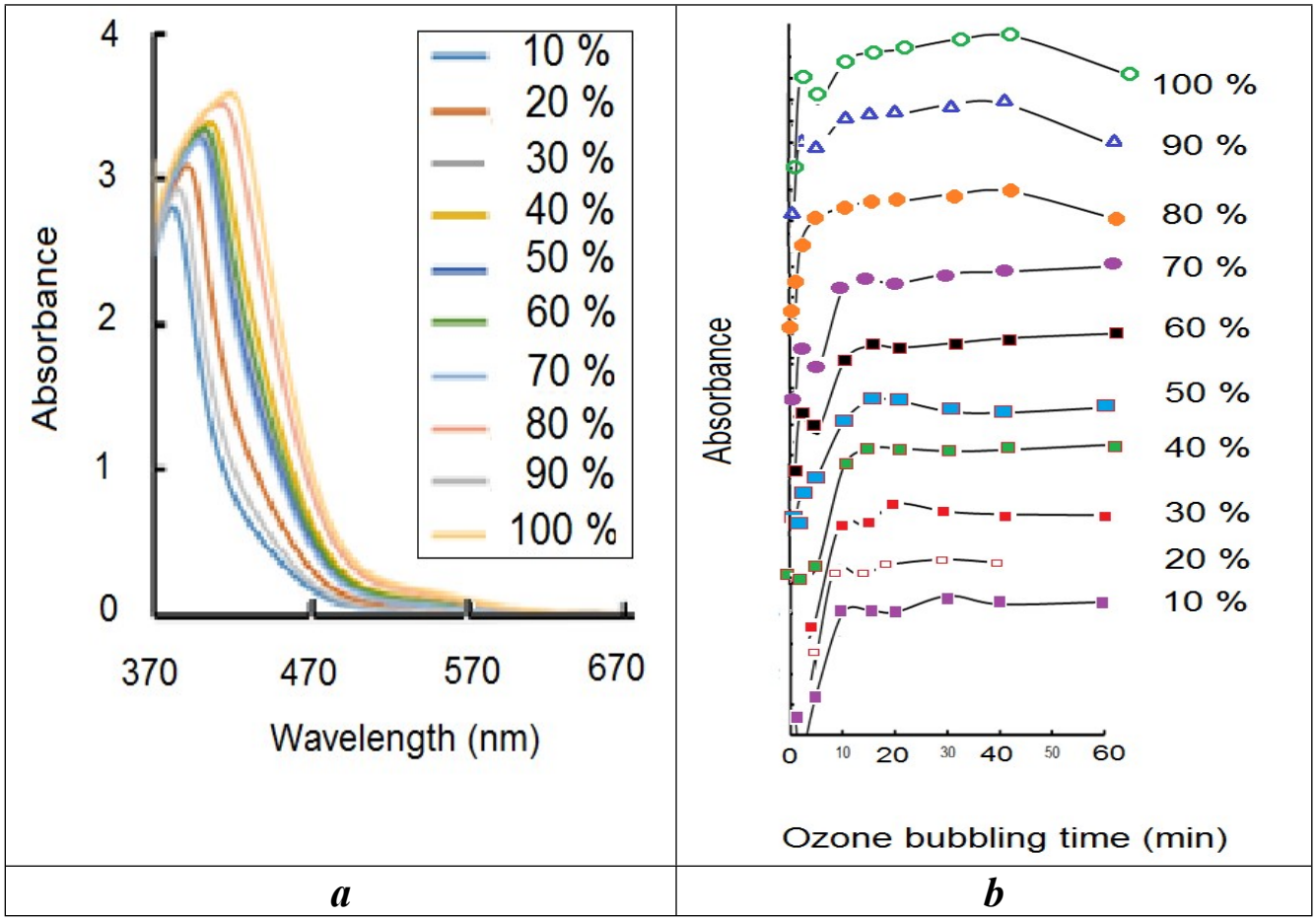
Ozone determination by titration of the KI solution

Ozone was titrated by iodometry. For this purpose,, ten samples of 200 mL potassium iodide solution (KI) were prepared by dissolving 0.5 g KI and 0.05g of potassium iodate (KIO_3) in 200 mL distilled water. Each samples was acidified with 10 mL of 1M HCl and then mixed with 7.8 mL of 0.1 M sodium thiosulfate ($Na_2S_2O_3$) (dark yellow solution). All samples were ozonized for five minutes at different ozone concentrations (10-100%) and then analyzed by UV-Vis spectrophotometry. A 1 mL amount of starch indicator was added to the solution (blue) and titrated was achieved with 0.1M $Na_2S_2O_3$ until the appearance of the pale yellow color. The mole number $n(O_3)$ and mass flow, D_{mass}, were calculated from the consumed volume of sodium thiosulphate, V ($S_2O^{2-}_3$)

$$n(O_3) = \frac{\left[S_2O^{2-}_3\right]V\left(S_2O^{2-}_3\right)}{2}$$

$$D_{mass} = \frac{n(O_3) * 48\ g/mol}{\Delta t}$$

1. *Ozone determination by titration of the KI solution*



a ***b***

Fig. S5. UV-Vis absorbance spectra of ozone in KI solution (**a**) and absorbance evolution as a function of ozone proportion in the bubbling air (%) (**b**).

DCF ozonation kinetics

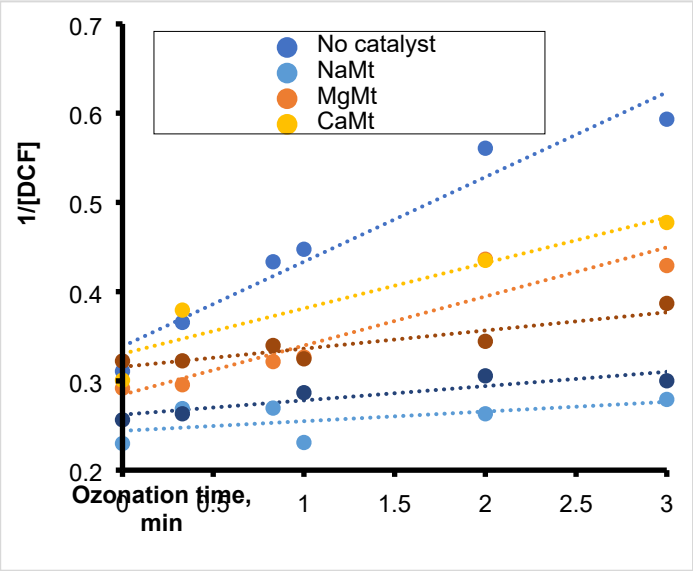
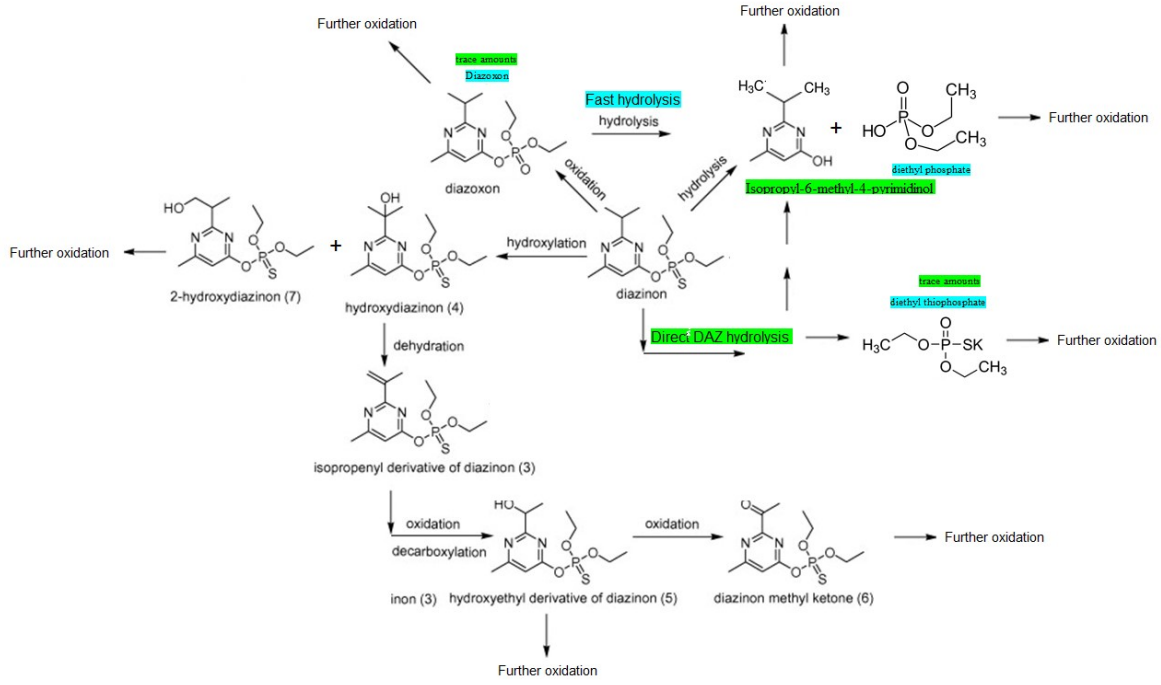
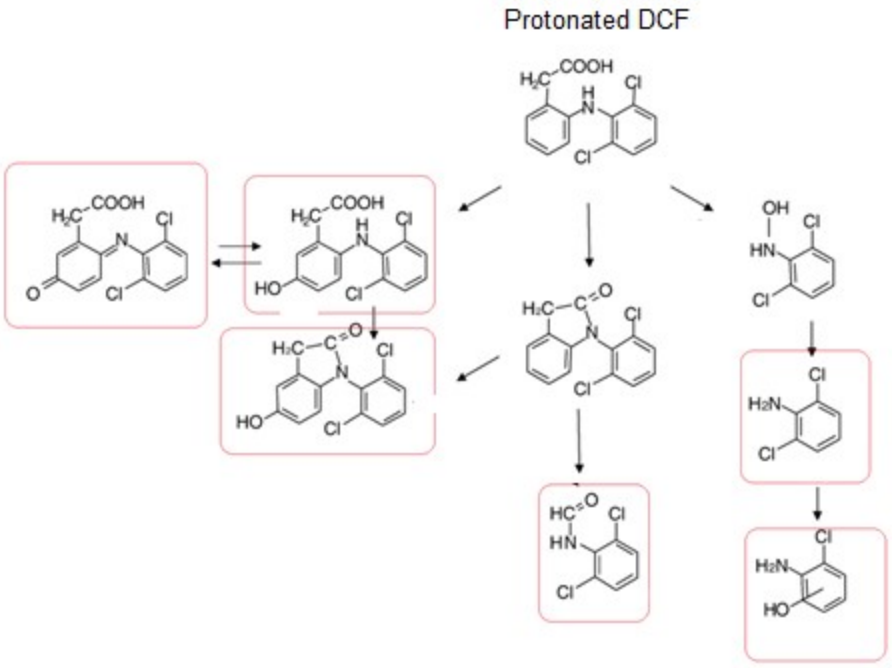


Fig. S6. 2nd-order kinetics of DCF catalytic ozonation.

Possible reaction pathways of ozonation based on a synthetic analysis of the literature



Scheme S1. Synthetic illustration of simultaneous degradation pathways in diazinon ozonation.



Scheme S2. Synthetic illustration of simultaneous degradation pathways in Diclofenac-Na ozonation. The most predominant DCF intermediates are presented in red frames.