Comptes Rendus
Chimie
Supplementary material to the article available at:
https://doi.org/10.5802/crchim.167

Supplementary material: Efficient degradation and mineralization of diclofenac in water on ZnMe (Me: Al; Co; Ga) layered double hydroxides and derived mixed oxides as novel photocatalysts

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Section S1

In brief, the aqueous samples were first centrifuged using a 0.22 μm nylon filter, after which a volume of 3 μl was injected on a Kinetex® XB-C18 column (150 × 2.1 mm, 1.7 μm particles; Phenomenex, the Netherlands) using an Agilent 1290 chromatographic system (Agilent, Santa Clara, USA). The mobile phases were (A) 0.1% (v/v) of formic acid in ultra-pure milli-Q water and (B) 0.1% (v/v) of formic acid in 90/10 (v/v) methanol/ultra-pure milli-Q water. An elution gradient was used for the separation as follows: start 5% B (1 min), then to 100% B in 10 min, keep 3 min, then back to 5% B for re-equilibration, keep 4 min. The flow rate was 0.4 mL/min and the temperature of the column 40 °C. The analytes were ionized using an Agilent Jet Stream ion source and the formed ions were detected by an Agilent 6530 QTOF MS. The drying and sheath gas temperatures were 300 and 350 °C, respectively. The drying and sheath gas flows were 8 and 11 L/min, respectively. The nebulizer pressure was 35 psig. The analysis was performed in both negative and positive ionization mode, with capillary voltage, nozzle voltage and fragmentor voltage set at 3000 V, 0 V and 120 V, respectively. The QTOF MS was continuously calibrated using a mixture of trifluoro-acetic acid, purine and HP-921, giving reference masses m/z of 121.0508 and

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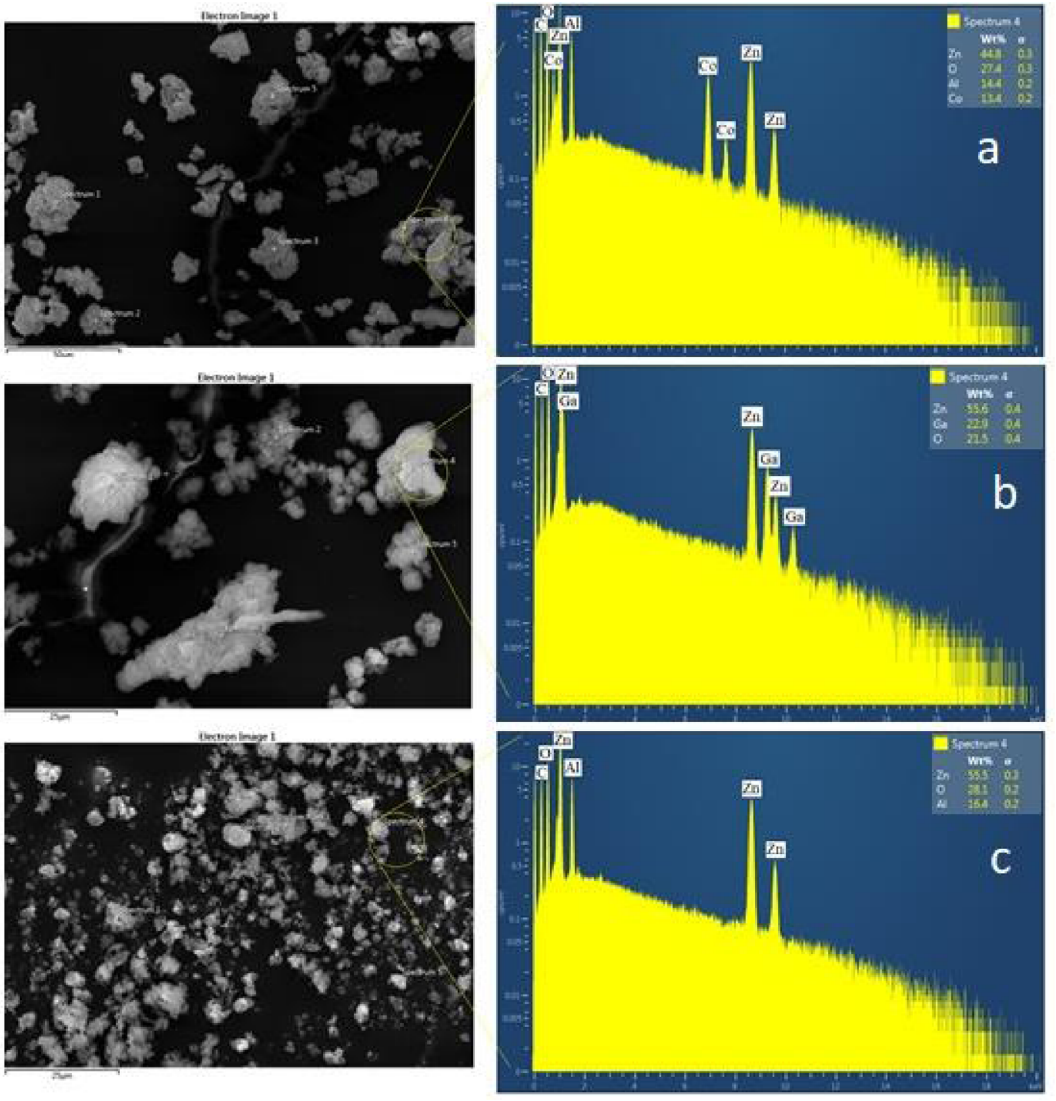
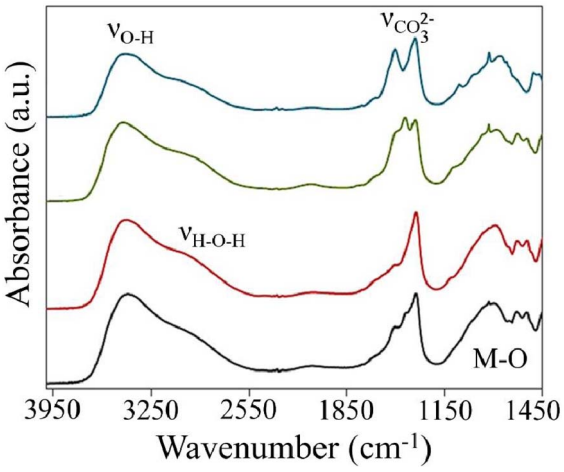
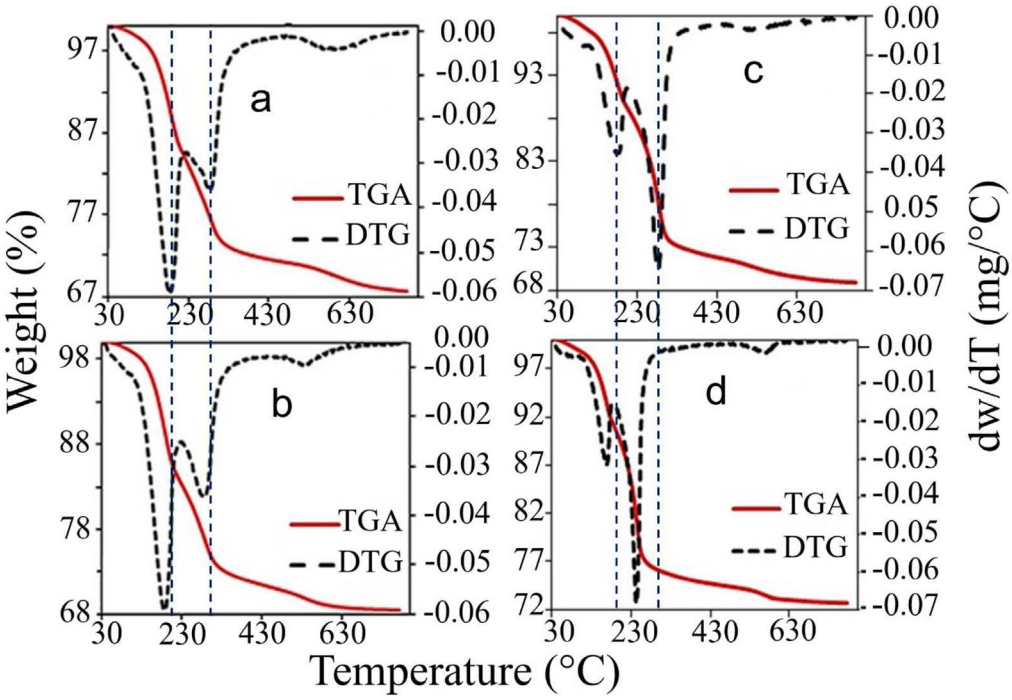


Supplementary Figure S2. EDX results of (a) ZnCo, (b) ZnGa, (c) $ZnAl_2$.

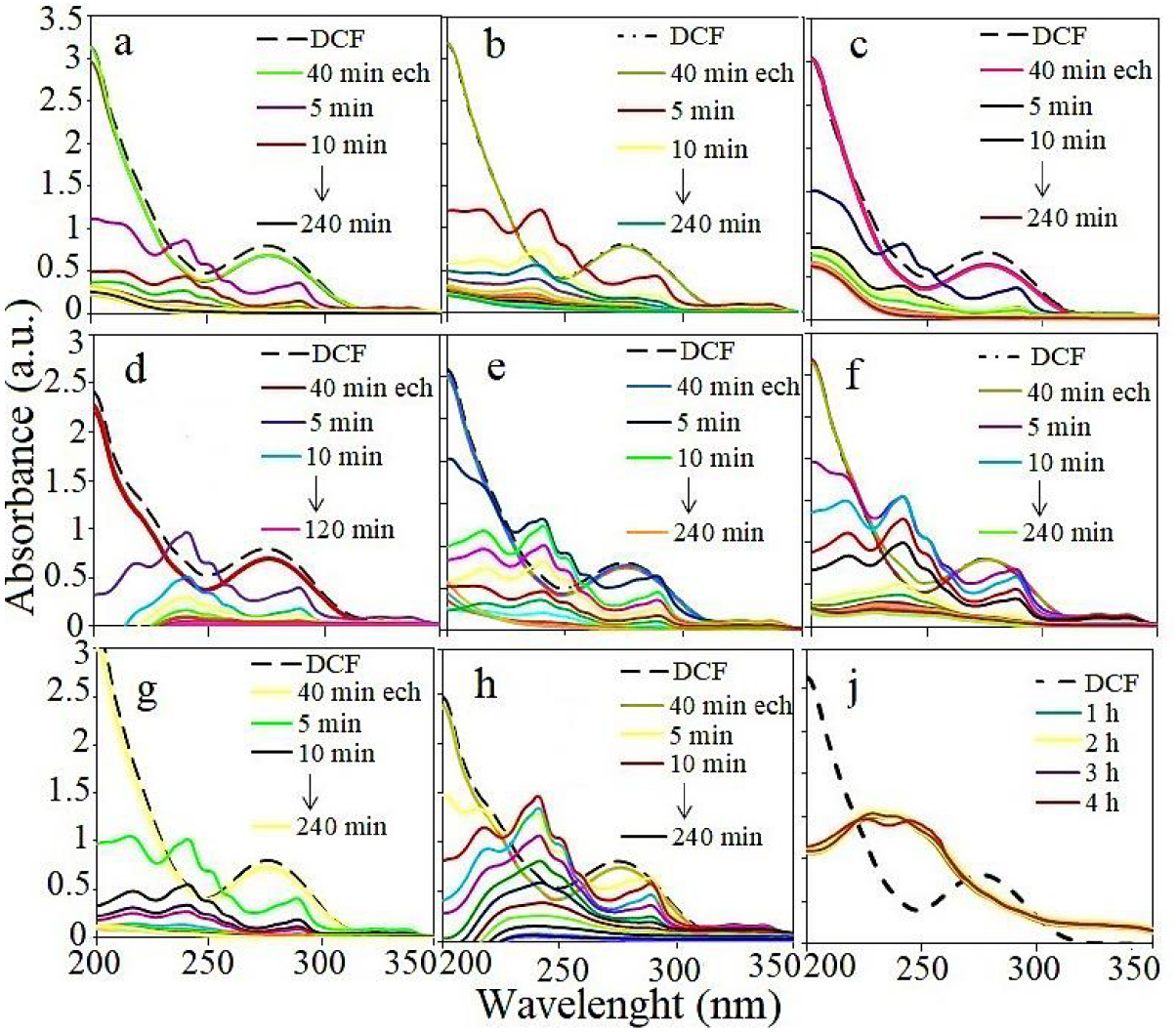
922.0098 in positive and 112.9855 and 966.0007 in negative mode, respectively). Mass-Hunter (Agilent, v B.06.00) and Mass-Profiler Professional (Agilent, v12.5) were used for data analysis and data mining. Identical molecular features between samples were aligned using a time window of 0.2 min and mass difference tolerance of 20 ppm. Further, molecular features which had trends that relate to chemical degradation were selected. Such features had an increasing signal (formation), decreasing signal (degradation) or complex pattern (formation and degradation combined) trend. The Molecular Formula Generator algorithm (MFG, Agilent) was used for the identification of features identified with Mass-Hunter. The results were the manually checked for isotope pattern, mass accuracy, and isotope spacing for the confirmation of the compound identity.



Supplementary Figure S3. DRIFT spectra of (■) $ZnAl_2$, (■) ZnCo, (■) $ZnAl_3$, (■) ZnGa.



Supplementary Figure S4. TG-DTG profiles of: (a) $ZnAl_2$, (b) ZnCo, (c) $ZnAl_3$, (d) ZnGa.



Supplementary Figure S5. UV–Vis profiles of DCF photodegradation by solar-light on: (a) $ZnAl_2$, (b) ZnCo, (c) $ZnAl_3$, (d) ZnGa, (e) $ZnAl_2$-750, (f) ZnCo-750, (g) $ZnAl_3$-750, (h) ZnGa-750, (i) blank.

Supplementary Table S6. DCF photodegradation products and intermediates identified by LC-MS analyses with the intermediates described as group: S1 for DCF transformation under solar photolysis; S2 for DCF photodegradation on ZnCo by UV light; S3 for DCF photodegradation on ZnCo by solar light. Catalyst dose 1 g/L and DCF concentration of aqueous solution 0.025 g/L

Measured m/z	Retention time, min	Predicted formula	System[a]
296.0175	8.06	DCF	S1, S2, S3
310.1021	6.61	$C_{14}H_9Cl_2NO_3$	S1, S2
297.2645	8.54	$C_{14}H_{12}Cl_2NO_2$	S1
275.9566	8.06	$C_{14}H_{10}ClNO_3$	S1, S2
280.1457	8.36	$C_{14}H_{11}Cl_2NO$	S1
278.0074	8.06	$C_{14}H_9Cl_2NO$	S1, S2, S3
259.20397	6.98	$C_{14}H_{10}ClNO_2$	S1, S2, S3
241.1567	5.33	$C_{14}H_{11}NO_3$	S1, S2, S3
227.2169	10.53	$C_{14}H_{13}NO_2$	S1, S2, S3
255.0527	5.54	$C_{14}H_9NO_4$	S1
255.0783	4.36	$C_{14}H_9NO_4$	S1
255.255	7.11	$C_{14}H_9NO_4$	S1
312.1765	8.00	$C_{14}H_{11}Cl_2NO_3$	S2
312.2071	9.80	$C_{14}H_{11}Cl_2NO_3$	S2
225.2055	9.18	$C_{14}H_{11}NO_2$	S2, S3
282.0071	6.79	$C_{13}H_9Cl_2NO_2$	S1, S3
246.2131	8.94	$C_{13}H_9ClNO_2$	S2
268.1943	8.91	$C_{13}H_{11}Cl_2NO$	S1, S2, S3
266.2187	8.09	$C_{13}H_9Cl_2NO$	S1, S2, S3
280.1381	8.07	$C_{13}H_7Cl_2NO_2$	S1, S2
252.1436	3.09	$C_{13}H_{11}Cl_2N$	S1, S2, S3
211.1563	5.90	$C_{13}H_9NO_2$	S1
215.0493	5.46	$C_{13}H_{10}ClN$	S1, S2, S3
282.1656	3.37	$C_{14}H_{13}Cl_2NO$	S3
261.1691	7.08	$C_{14}H_{12}ClNO_2$	S3
197.1406	5.40	$C_{13}H_{11}NO$	S3
162.1054	6.43	$C_6H_5Cl_2N$	S3
134.1008	7.93	$C_4H_6O_5$	S3
174.1351	7.03	$C_6H_6O_6$	S3
116.0845	3.743	$C_6H_{12}O_2$	S3
128.0932	3.71	C_6H_5ClO	S3
118.0783	8.07	$C_4H_6O_4$	S3
147.0889	3.36	$C_6H_4Cl_2$	S3
178.135	4.25	$C_6H_5Cl_2NO$	S2, S3
177.1314	4.31	$C_6H_2Cl_2O_2$	S2, S3
112.5082	3.20	C_6H_5Cl	S2, S3
163.1125	5.77	$C_6H_4Cl_2O$	S2, S3

(continued on next page)

Supplementary Table S6. (continued)

Measured m/z	Retention time, min	Predicted formula	System[a]
179.0925	3.63	$C_6H_4Cl_2O_2$	S2, S3
238.1381	10.78	$C_{12}H_9Cl_2N$	S1, S2, S3
190.1681	8.15	$C_7H_5Cl_2NO$	S2, S3
168.1154	5.78	$C_8H_8O_4$	S2, S3
140.1017	4.12	$C_7H_8O_3$	S2, S3
247.8903	8.20	$C_{13}H_{10}ClNO_2$	S3
227.1401	5.19	$C_{13}H_9NO_3$	S1

[a]S1: DCF transformation under solar photolysis; S2: DCF photodegradation on ZnCo by UV light; S3: DCF photodegradation on ZnCo by solar light; catalyst dose 1 g/L and DCF concentration of 0.025 g/L.